

Pyrolysis of Azidomanganese(III) Porphyrin Affording
Nitridomanganese(V) Porphyrin

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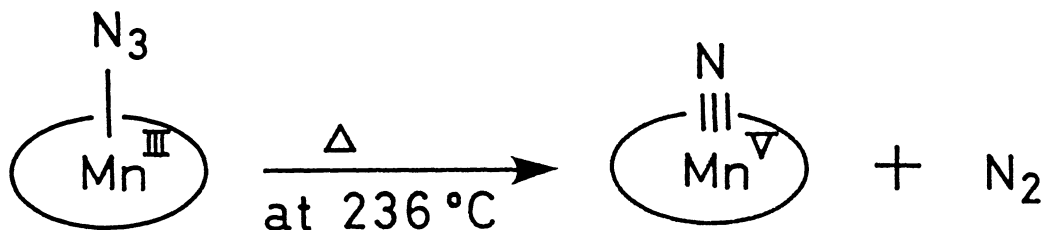
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Azidomanganese(III) *meso*-tetraphenylporphyrin, $\text{Mn}^{\text{III}}(\text{tpp})\text{N}_3$,
in the solid state was pyrolyzed around 236 °C to yield nitrido-
manganese(V) *meso*-tetraphenylporphyrin, $\text{Mn}^{\text{V}}(\text{tpp})\text{N}$.

Azidomanganese(III) porphyrins in organic solvents are photooxidized to yield corresponding nitridomanganese(V) porphyrins.¹⁻³⁾ These photoreactions proceed with the break of N-N₂ bond of the coordinated N₃⁻ ligand followed by the liberation of dinitrogen gas, i.e., the reaction is an intramolecular oxidation-reduction. This result suggests the occurrence of a similar intramolecular oxidation-reduction of azidomanganese(III) porphyrins in the solid state at high temperatures. We report here the first example of the pyrolysis of azidomanganese(III) porphyrin in the solid state to yield nitridomanganese(V) porphyrin. Nitridomanganese(V) porphyrin has a potential nitrogen activity to give aza analogue of epoxidation like aziridine from cyclooctene.²⁾

The $\text{Mn}^{\text{III}}(\text{tpp})\text{N}_3$ complex has electronic spectral bands at 477, 590, and 630 nm in toluene.³⁾ The powder of $\text{Mn}^{\text{III}}(\text{tpp})\text{N}_3$ was heated at 250 °C for 5 h under 10⁻³-10⁻⁵ Torr (1 Torr ≈ 133.3 Pa). A small amount of $\text{Mn}^{\text{III}}(\text{tpp})\text{N}_3$ was sublimed during the pyrolysis. A toluene solution of the product, prepared on a vacuum line, has main electronic spectral bands at 421 and 533 nm and minor bands at 435, 524, 566, and 602 nm. The main former bands agree with those of $\text{Mn}^{\text{V}}(\text{tpp})\text{N}$ prepared by the oxidation of $\text{Mn}^{\text{III}}(\text{tpp})\text{Cl}$ with NaOCl in the presence of ammonia.⁴⁾ The minor latter bands are ascribed to $\text{Mn}^{\text{II}}(\text{tpp})$, which was ascertained by its characteristic ESR signals around g = 6 at 77 K.³⁾ The evolution of dinitrogen gas was confirmed by EI-mass spectral measurements that showed molecular nitrogen- and nitrogen atom-characteristic bands at m/e = 28 and 14 respectively. Thermogravimetric measurements showed that the pyrolysis proceeds around 236 °C. The loss in weight by the pyrolysis was larger than the expected loss by liberated nitrogen gas, which is due to the sublimation of a small amount of $\text{Mn}^{\text{III}}(\text{tpp})\text{N}_3$ and the formation of a trace amount of $\text{Mn}^{\text{II}}(\text{tpp})$.⁵⁾ The IR spectrum of $\text{Mn}^{\text{III}}(\text{tpp})\text{N}_3$ (KBr pellet) has a characteristic band at 2036 cm⁻¹ of the coordinated N₃⁻ ligand. By the pyrolysis, the band disappeared with a concomitant appearance of a new band at 1048 cm⁻¹ which is ascribed to the stretching vibration of Mn≡N bond. The product was chromatographed twice on

alumina (neutral, grade I) using dichloromethane and then using 30% ethanol-benzene as eluents, followed by recrystallization with benzene-hexane and drying at 150 °C in vacuo. The result of elemental analysis of the red-purple complex obtained in 65% yield agreed with the empirical formula $C_{44}H_{28}N_5Mn$ of the nitrido complex. Anal. Found: C, 77.73; H, 4.16; N, 9.92%. Calcd for $Mn^V(tpp)N$: C, 77.53; H, 4.14; N, 10.27%.⁶⁾ The $Mn^V(tpp)N$ complex is sublimed around 280 °C.⁷⁾



These results show that the $Mn^{III}(tpp)N_3$ complex is pyrolyzed around 236 °C affording mainly the $Mn^V(tpp)N$ complex and a trace amount of $Mn^{II}(tpp)$.⁸⁾ The pyrolysis is a new way to prepare the nitridomanganese(V) porphyrin complex.⁹⁾

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References

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- 4) J. W. Buchler, C. Dreher, and K. L. Lay, Z. Naturforsch., B, 37, 1155 (1982).
- 5) $Mn^{II}(tpp)$ is unstable in air.
- 6) Recrystallization with dichloromethane-hexane as a solvent afforded a product containing 2-4% Cl which was not removed even by drying at 150 °C in vacuo.
- 7) $Mn^V(tpp)N$ is also pyrolyzed around 280 °C to yield $Mn^{II}(tpp)$.
- 8) The pyrolysis of an analogous complex, $Cr^{III}(tpp)N_3$, affords $Cr^V(tpp)N$. However, some complex different from $Cr^V(tpp)N$ is also yielded depending on the temperatures and the time of the pyrolysis.
- 9) The $[Fe(tpp)]_2N$ complex has been prepared by refluxing a xylene solution of $Fe^{III}(tpp)N_3$. D. A. Summerville and I. A. Cohen, J. Am. Chem. Soc., 98, 1747 (1976).

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