CHEMISTRY LETTERS, pp. 257-260, 1988.

Facile Preparation of Manganese(II) Tetraphenylporphyrin by the Pyrolysis of Dimethoxomanganese(IV) Tetraphenylporphyrin

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Manganese(II) tetraphenylporphyrin, Mn^{II}(tpp) (tpp = *meso*-tetraphenylporphinato), was afforded by the pyrolysis of $Mn^{IV}(tpp)(OCH_3)_2$ at ≈180 °C under 10^{-4}–10^{-5} Torr (1 Torr ≈ 133.3 Pa). The pyrolysis of $Mo^{V}O(tpp)OR$ (R = CH_3, C_2H_5) in the solid state yielded $Mo^{IV}O(tpp)$.

Manganese(II,III) porphyrin chemistry provides much important information on biomimetic reactions relevant to iron systems such as hemoglobin, myoglobin, and cytochrome.[1] However, preparation of manganese(II) porphyrins in the solid state is relatively difficult as compared with that of manganese(III,IV) porphyrins.

In this communication, a facile preparation of Mn^{II}(tpp) by pyrolysis of $Mn^{IV}(tpp)(OCH_3)_2$ in the solid state is reported. The pyrolysis of $Mo^{V}O(tpp)OCH_3$ is also reported for comparison with the reaction of $Mn^{IV}(tpp)(OCH_3)_2$ although the preparation of $Mo^{IV}O(oep)$ (oep = 2,3,7,8,12,13,17,18-octaethylporphinato) by pyrolysis of $Mo^{V}O(oep)OCH_3$ has been described in a dissertation.[2] These synthetic methods require no reducing agents and solvents. Manganese(II) porphyrins have been prepared by the reduction of manganese(III) porphyrins with sodium borohydride[3] or $Cr(acac)_2$[4] in organic solvents.

Absorption spectra were recorded on a Hitachi 808 spectrophotometer. X-Band ESR spectra were recorded on a JEOL JES-FE1X spectrometer operating at 100 kHz modulation. Infrared spectra of liberated gases were measured with a Hitachi 270-50 spectrophotometer using a 10-cm cell with NaCl windows. A NEVA NAG-515 mass filter was used to record temperature-programmed desorption (TPD) mass spectra. Thermogravimetric analyses (TG) were carried out on a Cahn 2000 electrobalance under 17 Torr argon atmosphere. Toluene, purified by a usual method[5] and stored over activated 4A Molecular Sieves in a glass vessel on a vacuum line, was deaerated by repeated freeze-thaw cycles before preparation of sample solutions. Pyrolysis of $Mn^{IV}(tpp)(OCH_3)_2$ was carried out under 10^{-4}–10^{-5} Torr using an electric furnace. The metallotetraphenylporphyrins, $Mn^{IV}(tpp)(OCH_3)_2$[6] and $Mo^{V}O(tpp)OCH_3$,[7] were prepared according to the methods given in literatures. Chromotropic acid dissolved in 50%(w/w) sulfuric acid was used to detect formaldehyde.[8]

$Mn^{IV}(tpp)(OCH_3)_2$ in the solid state was heated at 220 °C for 2 h under 10^{-5}

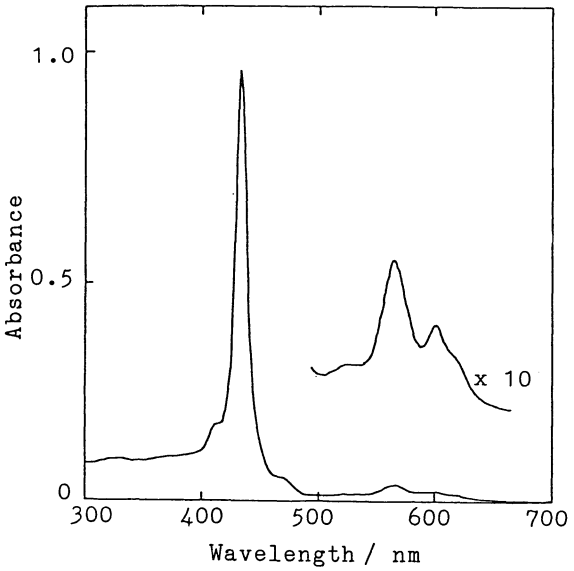

Fig. 1. Visible absorption spectrum of the pyrolyzed product of $Mn^{IV}(tpp)(OCH_3)_2$ in toluene at 25 °C.

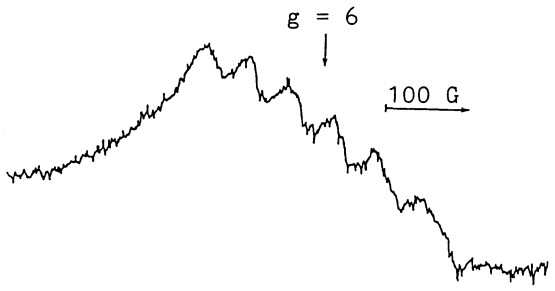

Fig. 2. ESR spectrum of the pyrolyzed product of $Mn^{IV}(tpp)(OCH_3)_2$ in toluene at 77 K.

Torr. The pyrolyzed product, dissolved in toluene, showed absorption bands at 435, 524, 566, and 602 nm at 25 °C as illustrated in Fig. 1. These bands are identical with those of $Mn^{II}(tpp)$ synthesized independently.[9] $Mn^{IV}(tpp)(OCH_3)_2$ in toluene shows no ESR signal at 77 K. However, the pyrolyzed product exhibited an ESR signal resolved into six lines around g = 6 as shown in Fig. 2. The ESR signal is characteristic of a high-spin (S = 5/2) d^5 configuration of manganese(II) porphyrins. The ESR and the absorption spectral measurements confirmed the formation of $Mn^{II}(tpp)$ by the pyrolysis of $Mn^{IV}(tpp)(OCH_3)_2$ in the solid state. The formation of $Mn^{II}(tpp)$ was supported by the elemental analysis of the pyrolyzed product. Anal. Found: C, 78.69; H, 4.19; N, 8.17%.[10] Calcd for $Mn^{II}(tpp)$ ($C_{44}H_{28}N_4Mn$): C, 79.15; H, 4.23; N, 8.39%.

The TG showed that the pyrolysis of $Mn^{IV}(tpp)(OCH_3)_2$ proceeded at temperatures above ≈180 °C. The weight-loss caused by the pyrolysis corresponds nearly to the expected mass for two methoxyl groups in one molecule of $Mn^{IV}(tpp)(OCH_3)_2$.

$$Mn^{IV}(tpp)(OCH_3)_2 \xrightarrow[\text{in solid}]{\Delta\ (180\ ^\circ C)} Mn^{II}(tpp) \qquad (1)$$

Liberated gases were detected by IR, EI-mass, TPD-mass spectral measurements. The infrared spectrum of the gases showed the bands at 3712, 2972, 2808, 1748, and 1036 cm^{-1} as shown in Fig. 3. These bands could be assigned to O-H, C-H, C-H, C=O, and C-O stretching vibrations, respectively. Neat methanol gas has IR bands at 3712, 2972, and 1036 cm^{-1}. Formaldehyde gas formed by heating paraformaldehyde at 120 °C has the bands at 2808 and 1748 cm^{-1}. The results of infrared spectral measurements suggest the formation of methanol and formaldehyde by the pyrolysis of $Mn^{IV}(tpp)(OCH_3)_2$.

EI-mass spectral measurements supported the formation of methanol and formaldehyde, i.e., liberated gases showed main signals at m/e = 28, 29, 30, 31,

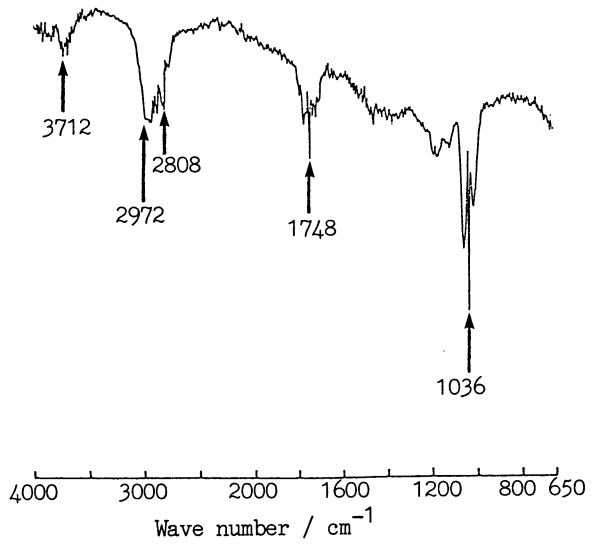

Fig. 3. IR spectrum of the gases liberated by the pyrolysis of $Mn^{IV}(tpp)(OCH_3)_2$.

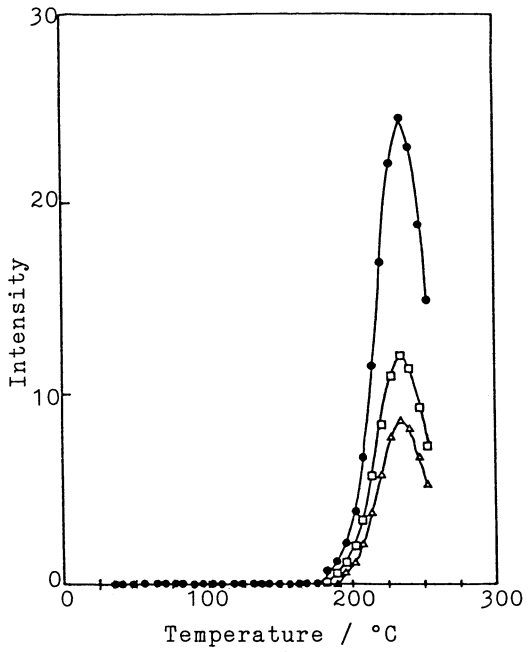

Fig. 4. TPD-mass spectra of the gases liberated by the pyrolysis of $Mn^{IV}(tpp)(OCH_3)_2$. Symbols ●, □, and △ indicate intensities measured at m/e = 29, 30, and 32, respectively. The spectral features at m/e = 28 and 31 are the same as those shown in the figure.

and 32 in which the signals at 29, 31, and 32, and the signals at 28, 29, and 30 were ascribed to those of methanol and formaldehyde, respectively. Formaldehyde was also detected by the chromotropic acid method; chromotropic acid solution dissolving the liberated gases showed the absorption band at 570 nm.

The pyrolysis of $Mn^{IV}(tpp)(OCH_3)_2$ was followed by the TPD-mass spectral measurements to detect the species liberated from $Mn^{IV}(tpp)(OCH_3)_2$ at appropriate temperatures during the pyrolysis. The TPD-mass spectra showed main signals at m/e = 28, 29, 30, 31, and 32 at temperatures from 180 to 256 °C. The signals are the same as those observed in the EI-mass spectral measurements. The ratios of the signal intensities of these mass numbers did not change during the pyrolysis, indicating invariance of the pyrolyzed products at the temperatures, as shown in Fig. 4.

The pyrolysis of $Mo^{V}O(oep)OCH_3$ yields $Mo^{IV}O(oep)$ at 250 °C under 10^{-4} Torr.[2] Formation of $Mo^{IV}O(tpp)$ by the pyrolysis of $Mo^{V}O(tpp)OCH_3$ in the solid state around 260 °C under 10^{-4}–10^{-5} Torr was also confirmed. The visible absorption spectrum of the pyrolyzed product in toluene showed the bands at 430 and 556 nm at 25 °C which are consistent with the bands of $Mo^{IV}O(tpp)$ synthesized by the reduction of $Mo^{V}O(tpp)Cl$ with amalgamated zinc and purified by sublimation in vacuo.[11] $Mo^{V}O(tpp)OCH_3$ in toluene exhibited an ESR signal (g = 1.972) due to $^{94,96,98,100}Mo(V)(d^1)$ which is split into nine hyperfine lines by coupling with the four nitrogen atoms of the porphyrin ring. The pyrolyzed product from $Mo^{V}O(tpp)OCH_3$ showed no signal in toluene. The absence of an ESR signal supported the formation of an ESR-silent species, as is the case for the low-spin complex of $Mo^{IV}O(tpp)$. The elemental analysis of the pyrolyzed product

justified the formation of $Mo^{IV}O(tpp)$. Anal. Found: C, 72.69; H, 3.85; N, 7.48% Calcd for $Mo^{IV}O(tpp)$ ($C_{44}H_{28}N_4OMo$): C, 72.93; H, 3.89; N, 7.73%.

$$Mo^{V}O(tpp)OCH_3 \xrightarrow[\text{in solid}]{\Delta\ (260\ ^\circ C)} Mo^{IV}O(tpp) \qquad (2)$$

The pyrolysis of $Mo^{V}O(tpp)OCH_3$ proceeded above ≈260 °C to yield $Mo^{IV}O(tpp)$.[12] The weight-loss by the pyrolysis was larger than the expected weight due to concomitant partial sublimation of the product, $Mo^{IV}O(tpp)$. Although the mass spectral measurements and the chemical analysis using chromotropic acid suggested the formation of small amounts of methanol and formaldehyde during the pyrolysis of $Mo^{V}O(tpp)OCH_3$, the infrared spectra of liberated gases showed no significant bands. The gases liberated by the pyrolysis of $Mo^{V}O(tpp)OCH_3$ have not been characterized.

It has become apparent in this study that $Mn^{II}(tpp)$ and $Mo^{IV}O(tpp)$ are easily yielded by the pyrolyses of $Mn^{IV}(tpp)(OCH_3)_2$ and $Mo^{V}O(tpp)OCH_3$, respectively. Pyrolysis was found to be a useful method for preparation of unstable manganese(II) complexes.

We acknowledge Dr. Tsutomu Yamaguchi (Department of Chemistry) for many discussions on TG and TPD measurements and Akiko Yamazaki (Research Institute for Catalysis) for EI-mass spectrometric measurements.

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(Received November 2, 1987)