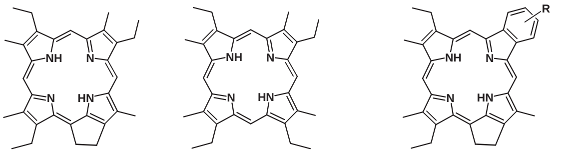
The First Experimental Demonstration of Benzoporphyrin Formation from Sedimentary Porphyrins

Shinya Nomoto,*[1] Mitsuru Satou,[1] Takahiro Yoshida,[1] Hajime Mita,[2] Gen Kumagai,[1] Kouichi Nomoto,[1]
Hideo Kigoshi,[1] and Yuichiro Kashiyama[3]
[1]*Department of Chemistry, University of Tsukuba, Tsukuba 305-8571*
[2]*Department of Life, Environment and Material Science, Fukuoka Instutute of Technology, Fukuoka 811-0295*
[3]*Department of Earth and Planetary Science, The University of Tokyo, Tokyo 113-0033*

(Received February 12, 2008; CL-080157; E-mail: nomoto@chem.tsukuba.ac.jp)

Etioporphyrin, one of the most common sedimentary porphyrins, was heated at 300 to 450 °C to investigate the diagenetic formation of benzoporphyrins. Chromic acid oxidation of the resulting products afforded maleimides, as well as phthalimides, indicating the formation of benzopyrrole units in the substrate. Isomer ratios of dimethylphthalimides formed during heating were in accordance with those obtained by chromic acid oxidation of the Cretaceous/Tertiary sediments at Rumoi, Hokkaido, which suggests that alkylporphyrins could be transformed into benzoporphyrins in sediments.

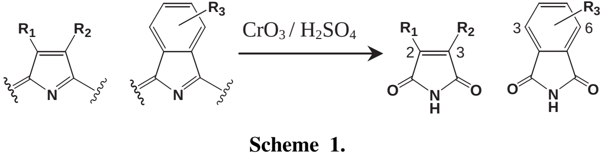
Sedimentary porphyrins are mostly assigned to the diagenetic products of chlorophylls from past primary producers and hence represent a valuable resource of information in paleobiological and paleoenvironmental studies.[1] Benzoporphyrins have been found as minor components of sedimentary porphyrins,[2] and a vinyl side chain of chlorophyll molecules has been considered to take part in the formation of the benzene ring at the early stage of diagenesis.[3] In our previous work, several vinyl porphyrins were shown to have the ability to form benzopyrrole units, which might explain the presence of benzoporphyrins in immature sedimentary organic matter (Chart 1).[4]



Typical sedimentary porphyrins A benzoporphyrin

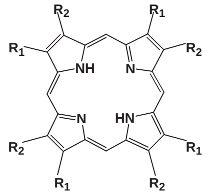
Chart 1.

In the course of our investigation on chlorophyll diagenesis, we have analyzed porphyrins or their fragments bound to insoluble matter in sediments by the chromic acid oxidation method, which transforms the pyrrole units of porphyrins into maleimides and benzopyrrole units, if present, into phthalimides (Scheme 1).[5] In the analysis of a stratigraphic sequence of sediments, the abundances of oxidatively extracted phthalimides have been found to increase with increasing maturity of the organic matter, suggesting that the formation of benzoporphyrins takes place from sedimentary porphyrins with no unsaturated side chains.[6] It is important to demonstrate that benzopyrrole units can be produced from an ethylmethylpyrrole unit of major sedimentary porphyrins, since most of the benzoporphyrins found in sediments are considered to be produced in mature stratigraphic zones. We performed heating experiments of etioporphyrin and several other alkylporphyrins for this purpose.



Scheme 1.

Octaethyl-, etio-, and octamethylporphyrins (ca. 0.1 mg) were heated at 300 to 450 °C for up to 360 h in a degassed sealed tube. The products were oxidized with 10% CrO_3 in 25% H_2SO_4 (1 mL) at 0 °C for 1 h and at room temperature for 1 h to afford a mixture of maleimides and phthalimides. These products were then extracted with benzene and analyzed by GC-MS equipped with an FFAP capillary column (60 m × 0.25 mm i.d.) Identification and quantification of the products were performed by comparison of the GC-MS data with those of authentic samples (Chart 2).



Octaethylporphyrin: $R_1 = R_2 = Et$
Etioporphyrin: $R_1 = Me$, $R_2 = Et$
Octamethylporphyrin: $R_1 = R_2 = Me$

Chart 2.

After heating, the porphyrins, which are soluble in several solvents, afforded insoluble products. Although heating seemed to cause serious degradation or polymerization of the porphyrins, maleimides and phthalimides were successfully detected after oxidation of the products, indicating that the alkylpyrrole and benzopyrrole moieties survived to some extent after heating. The total yield of maleimides and phthalimides detected in the heating of etioporphyrin at 300 °C for 72 h was about 0.4%. Unheated etioporphyrin afforded only 2-ethyl-3-methylmaleimide on chromic acid oxidation, while oxidation of the heated substrate yielded phthalimide, methyl-, ethyl-, and dimethylphthalimides as well as several maleimides, as shown in Figure 1. The results clearly indicate that the ethylmethylpyrrole units of etioporphyrin were

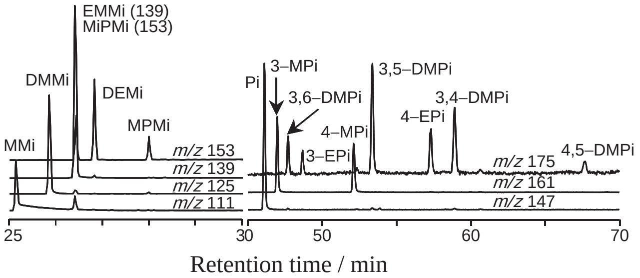


Figure 1. Mass fragmentograms of maleimides and phthalimides obtained by oxidation of etioporphyrin heated at 400 °C for 12 h. MMi: 3-methyl-maleimide, DMMi: 2,3-dimethylMi, EMMi: 2-ethyl-3-methyl-Mi, MiPMi: 2-methyl-3-isopropylMi, DEMi: 2,3-diethylMi, MPMi: 2-methyl-3-*n*-propylMi, Pi: phthalimide, MPi: methylPi, EPi: ethylPi, DMPi: dimethylPi.

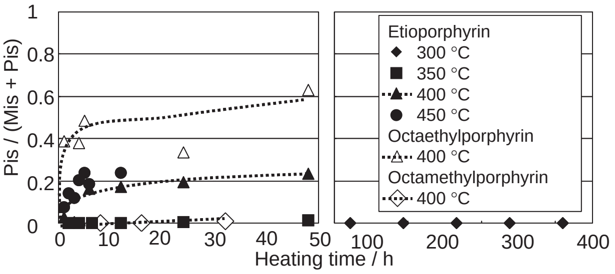


Figure 2. Time-course plot of phthalimides formation in heating experiments of etio-, octaethyl-, and octamethylporphyrins.

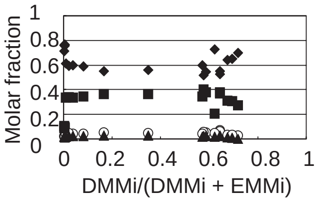


Figure 3. Plot of the molar fractions of phthalimide homologs formed from heated etioporphyrin against the demethylation index. ◆: Pi, ■: MPis, ▲: EPis, ○: DMPis. Abbreviations are shown in Figure 1.

converted into benzopyrrole units during the heating.

The ratios of phthalimides (Pis) to maleimides (Mis), expressed as Pis/(Mis + Pis), obtained during the heating of etio-, octaethyl-, and octamethylporphyrins are plotted against the reaction time in Figure 2. Efficient generation of benzopyrrole units in etioporphyrin was observed at 400 °C or above. From the results of the heating experiments of three porphyrins, the presence of an ethyl side chain was found to favor benzene ring formation, which was further confirmed by the fact that practically no phthalimides were obtained during the heating of porphine at 400 °C.

In Figure 3, the molar fractions of phthalimide and its homologs obtained during the heating of etioporphyrin are plotted against the extent of demethylation at the ethyl side chain, which represents thermal maturity of the porphyrin.[6] Heating of all the porphyrins, after chromic acid oxidation, afforded phthalimide, methylphthalimides, and ethyl- and dimethylphthalimides as minor products; no marked difference was observed among these results.

On the other hand, heating of each porphyrin respectively afforded a characteristic distribution of dimethylphthalimide (DMPi) isomers. Thus, 3,6- and 3,4-DMPis predominated in the products from octaethylporphyrin (the average molar fractions of 3,6- and 3,4-DMPis were 0.45 and 0.40, respectively), while 3,4- and 3,5-DMPis were the major products from etioporphyrin (Figure 4). In contrast, one of the major products from octamethylporphyrin was 4,5-DMPi (the average molar fraction of 4,5-DMPi was 0.50), which was the minor product generated from the other porphyrins. These results reveal that structural differences in the starting alkylporphyrins provide different profiles of thermal dimethylbenzopyrrole production.

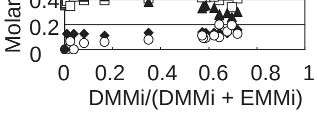


Figure 4. Plot of the molar fractions of DMPi isomers formed from etioporphyrin against the demethylation index. ◆: 3,6-DMPi, □: 3,5-DMPi, ▲: 3,4-DMPi, ○: 4,5-DMPi. Abbreviations are shown in Figure 1.

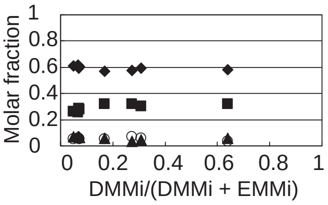


Figure 5. Plot of the molar fractions of phthalimide homologs extracted from the stratigraphic sequence of the Rumoi sediments against the demethylation index. Symbols are as in Figure 3.

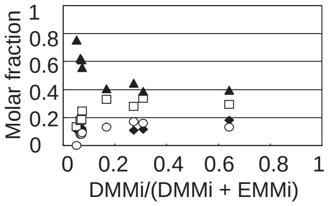


Figure 6. Plots of the molar fractions of DMPi isomers extracted from the stratigraphic sequence of the Rumoi sediments against the demethylation index. Symbols are as in Figure 4 and abbreviations are shown in Figure 1.

Dimethylphthalimides were then identified in the oxidative extracts of natural sediments, that is, the Cretaceous/Tertiary stratigraphic sequence of sediments at Rumoi, Japan. Thus, after washing of powdered sample (5.0 g) with a mixture (10 mL) of benzene and methanol (5:1, v/v) by sonication for five times, it was oxidized with 10% CrO_3 in 25% H_2SO_4 (10 mL) at 0 °C for 2 h and at room temperature for 2 h. The suspension was extracted five times with benzene (10 mL), and the extracts were concentrated carefully to 100 µL under a nitrogen flow and analyzed by GC-MS. The compositions of phthalimide homologs were found to be constant throughout the sequence, with their ratios in accordance with the results of the heating experiments (Figure 5). The isomer ratios of dimethylphthalimides in the Rumoi sediments[7] agreed well with those established in the heating products of etioporphyrin (Figure 6). Since the ethylmethylpyrrole unit constituting etioporphyrin is a most abundant structural component of sedimentary porphyrins, the results of the present study may indicate that phthalimides obtained by direct oxidation of the sediments originate from tetrapyrrole pigments of ancient photosynthetic organisms.

In conclusion, we have elucidated that the alkylpyrrole units of sedimentary porphyrins could be converted into benzopyrroles by the action of heat. We also provide the first evidence for the diagenetic production of benzoporphyrins from etioporphyrin on the basis of the coincidence of isomer ratios of dimethylphthalimides formed during the heating experiments with those found in the natural sediments. These findings may enable us to understand chlorophyll diagenesis leading to benzoporphyrin formation in mature stratigraphic zones.

We are grateful to Japan Oil, Gas, and Metals National Corporation for samples of Rumoi sediments.

References and Notes

1 Y. Kashiyama, M. Shiro, R. Tada, N. Ohkouchi, *Chem. Lett.* **2007**, *36*, 706, and references cited therein.
2 S. Ito, H. Uno, T. Murashima, N. Ono, *Tetrahedron Lett.* **2001**, *42*, 45, and references cited therein.
3 S. Kaur, M. I. Chicarelli, J. R. Maxwell, *J. Am. Chem. Soc.* **1986**, *108*, 1347.
4 M. Kozono, S. Nomoto, A. Shimoyama, *Chem. Lett.* **2002**, 470.
5 a) A. Shimoyama, K. Kozono, H. Mita, S. Nomoto, *Geochem. J.* **2001**, *35*, 365. b) S. Nomoto, H. Kigoshi, *Res. Org. Geochem.* **2005**, *20*, 31.
6 M. Kozono, S. Nomoto, H. Mita, A. Shimoyama, *Geochem. J.* **2001**, *35*, 225.
7 The concentrations of each DMPi were 2 to 20 pmol/g-rock.

Published on the web (Advance View) March 29, 2008; doi:10.1246/cl.2008.490