CHEMISTRY LETTERS, pp. 2411-2414 1994.

How Do Nitrogen Bases Accelerate the Decomposition of H_2O_2 in a Manganese Porphyrin Dimer Catalyst ? Quantitative Evaluation of the Base Effects by Its Axial Coordination vs. General-base Catalysis

Yoshinori NARUTA* and Masa-aki SASAYAMA†
Institute for Molecular Science, Myodaiji, Okazaki 444
†Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606-01

Kinetic analysis of the dismutation reaction of H_2O_2 with a cofacial manganese porphyrin dimer gave the separate evaluation of two roles of nitrogen bases on the decomposition of H_2O_2 and the axial coordination of bases enhances the reaction of H_2O_2 with the manganese porphyrin in 6.6 times larger than by a general-base catalysis.

The reaction of manganese porphyrin dimers having short Mn-Mn separations exhibits sharp contrast with that of the corresponding monomers in the dismutation of H_2O_2. We have demonstrated that the dimers are excellent catalysts for the dismutation of H_2O_2 to O_2.[1] Thus, this system is considered to be a good functional model of manganese catalases, which contain a nonheme-type manganese binuclear center in their

$$2H_2O_2 \xrightarrow{\text{Mn porphyrin dimer}} O_2 + 2H_2O$$

subunits.[2] Simple manganese porphyrins themselves are inert to H_2O_2 unless an appropriate base is present in the solution.[3a] In the reaction of a manganese porphyrin with H_2O_2, a nitrogen base is supposed to function in the following two modes[2] (Fig. 1): (1) As a general base catalyst, deprotonation of hydrogen peroxide to facilitate its coordination with the manganese ion, and (2) as an axial ligand, acceleration of the O-O bond cleavage of the Mn-O-O-H by its electron-pushing effect. In their modeling reaction, these two roles have never been separately and quantitatively evaluated in spite of their importance, presumably because the preferential formation of the inert six-coordinated complex at high base concentration makes the analysis difficult. The H_2O_2 disproportionation with manganese porphyrin *monomer* is rather slow process, even in the presence of a base.[3b] When one uses the manganese porphyrin dimers having a short metal separation could prevent the coordination of nitrogen bases inside the molecular cavity

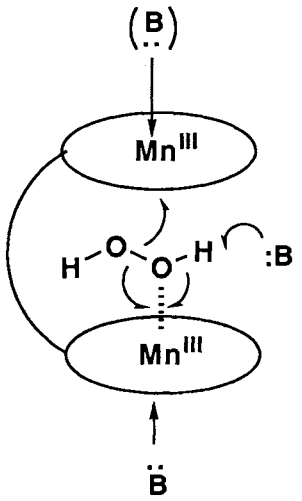
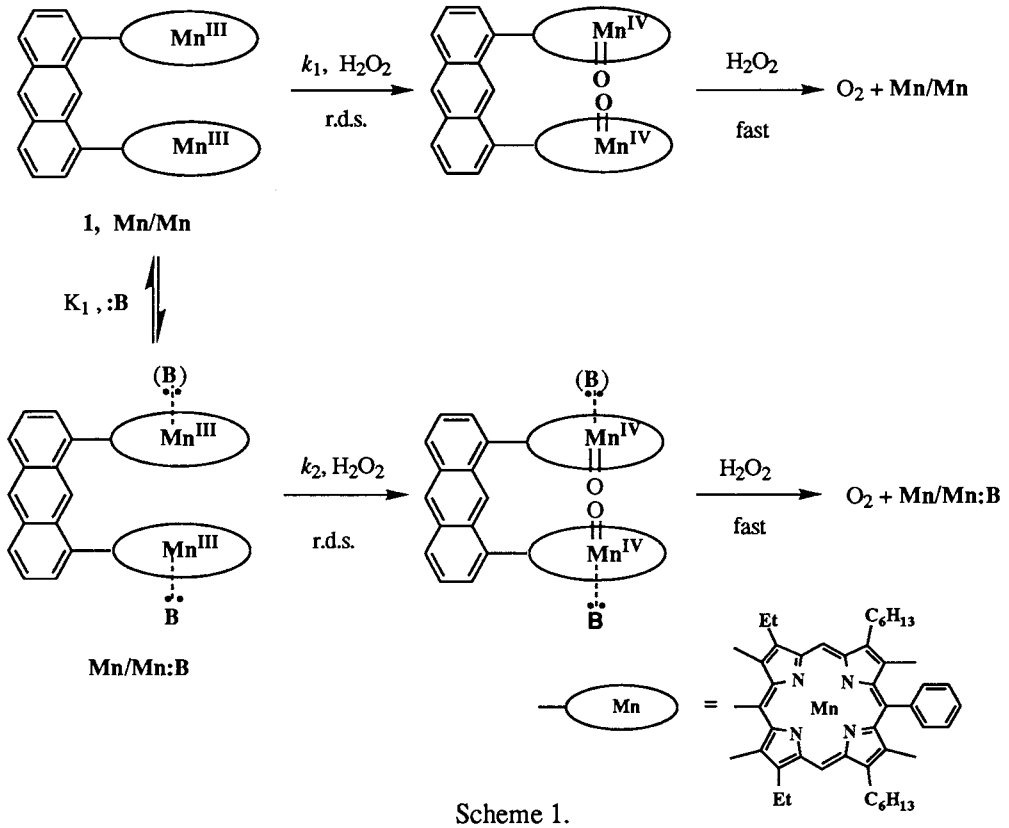


Fig. 1. Two roles of a nitrogen base in the reaction of H_2O_2 with a manganese porphyrin dimer.



Scheme 1.

sandwiched by two planar porphyrins. Thus, each manganese porphyrin in the dimer can form only the corresponding five-coordinated complex with a nitrogen base, while small H_2O_2 molecule can freely enter the cavity and can react with the two manganese ions. Fortunately, cofacial manganese porphyrin dimers[3] have following advantages over the reported ones on the evaluation of these base effects: The rate determining step of the H_2O_2 disproportionation with the manganese porphyrin dimers is the stage of the reaction of the initial H_2O_2 molecule with the $Mn(III)_2$ complex to form the corresponding $Mn(IV)_2$, because the successive two-electron oxidation of the second H_2O_2 molecule is rapid process.[1] Thus, one can easily determine the initial H_2O_2 reaction rate by monitoring the O_2 evolution by the dimer catalyst. In this paper, we describe the quantitative evaluation of the two effects of bases on the O-O bond cleavage and show the correlation between the decomposition rate of H_2O_2 and base pk_a values with use of 1,8-anthracene-linked manganese porphyrin dimer **1** as a catalyst (Scheme 1).

The effect of a nitrogen base as a general base catalyst was evaluated with use of several 2,6-disubstituted pyridine derivatives, which cannot coordinate to the manganese ions even at a high concentration.[5] The rate constant $k_1$was obtained by means of the quantitative determination of evolved oxygen.[6] As observed in Fig. 2, a good linear correlation between k_1 and pk_a of the pyridine derivatives[4] over a wide pk_a range proved this reaction to be the general-base catalyzed.[7] When one applies coordinative nitrogen bases to this reaction, one can expect two functions of the bases as shown above. Resultant velocities of oxygen evolution can be expressed according to the following equation, where **[Mn/Mn]** and **[Mn/Mn:B]** are the concentrations of the base-uncoordinated and coordinated manganese porphyrin dimers, respectively.

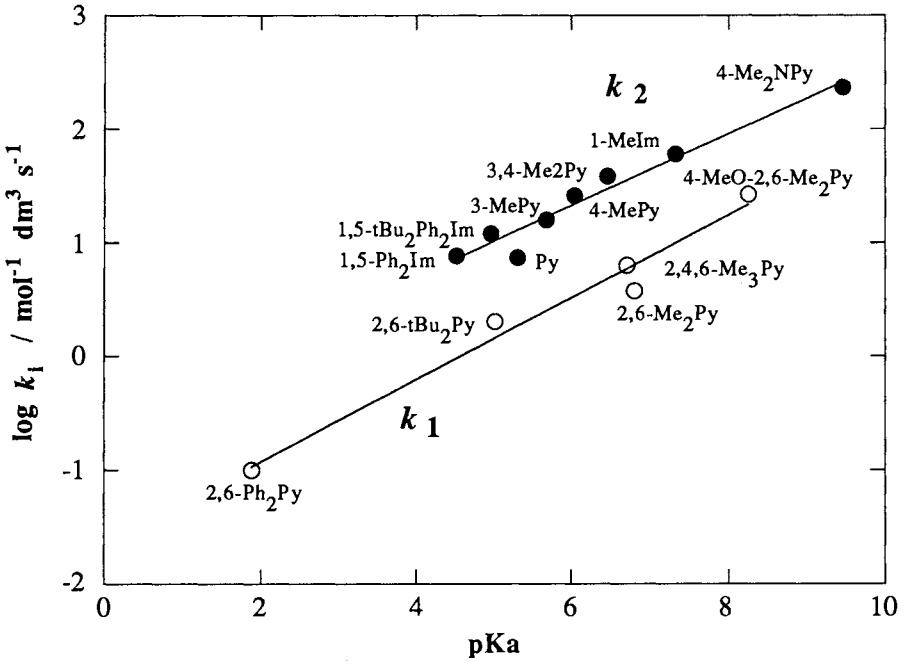


Fig. 2. Correlation between basicity of nitrogen bases and rate constants log k_i. For abbreviation of the base names, see Reference 11.

$$\frac{d[O_2]}{dt} = k_1[H_2O_2][\mathbf{Mn/Mn}] + k_2[H_2O_2][\mathbf{Mn/Mn:B}]$$

The first term expresses the rate simply accelerated by the general-base catalysis of the added nitrogen base. The second one shows the rate that affected by the axial coordination of the base coupled with the general base effect. At the given concentration of a base, the ratio between **[Mn/Mn]** and **[Mn/Mn:B]** can be estimated from the formation constant K_1 of an applied base concentration.[8] The unknown k_1 of the reaction containing a coordinating base can be evaluated according to the linear relationship between pK_a of the base and log k_1. Thus, k_2 can be determined for each coordinating nitrogen base and was plotted in Fig. 2. Good linear relationship between log k_2 and pK_a was also obtained. The rate enhancement factor k_2/k_1 by the axial coordination of a nitrogen base is estimated to be 6.6±1.7 irrespective of the base pKa. This leads that the electron-pushing effect of a base by the axial coordination is several times higher than the effect as a general-base catalyst irrespective to the base strength. Thus, the quantitative evaluation of the base effects can be attained by use of the sterically hindered manganese porphyrin dimer. The present proposal will be essential for the design or analysis of new artificial enzyme models, including heme catalase[9] and peroxidase.[10] Furthermore, these results are reminiscent of the presence of an appropriate basic residue around the active site of manganese catalases.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan under Grant Nos. 05209214, 05453030, and 05235225.

References

1) Y. Naruta and K. Maruyama, *J. Am. Chem. Soc.*, **113**, 3595 (1991); Y. Naruta, M. Sasayama, and K.

Maruyama, *Chem. Lett.*, **1992**, 1267.

2) Y. Kono and I. Fridovich, *J. Biol. Chem.*, **258**, 6015 (1983); G. S. Algood and J.J. Perry, *J. Bacteriol.*, **168**, 563 (1986); S. V. Khangulov, V. V. Barynin, and S. V. Antonyuk-Barynina, *Biochem. Biophysica Acta*, **1020**, 25 (1990); J. E. Penner-Harn, "Manganese Redox Enzymes," ed. by V. L. Pecoraro, VCH, New York (1992), p. 29.

3) P. Battioni, J. O. Renaud, J. F. Bartoli, M. Momenteau, and D. Mansuy, *Recl. Trav. Chim. Pays-Bas*, **106**, 332 (1987); P. Battioni, J. P. Renaud, J. F. Bartoli, M. Reina-Artiles, M. Fort, and D. Mansuy, *J. Am. Chem. Soc.*, **110**, 8462 (1988); P. N. Balasubramanian, E.S. Schmidt, and T.C. Bruice, *J. Am. Chem. Soc.*, **109**, 7865 (1987); R. Belal, M. Momenteau, and B. Meunier, *J. Chem. Soc., Chem. Commun.*, **1989**, 412.

4) A. Albert, "Physical Methods in Heterocyclic Chemistry," ed. by A. R. Katritzky, Academic Press, New York (1963), p. 1; A. Albert, "Physical Methods in Heterocyclic Chemistry," ed. by A. R. Katritzky, Academic Press, New York (1971), p. 1; E. F. V. Scriven, "Comprehensive Heterocyclic Chemistry," Vol. 2, ed. by A. R. Katritzky and C. W. Rees, Pergamon Press, Oxford (1984), p.165; M. R. Grimmett, *ibid.*, Vol. 5, p.373; D. H. Mcdaniel and M. Ozcan *J. Org. Chem.*, **33**, 1922 (1968); M. R. Charkrabarty, C. S. Handloser, and M. W. Mosher, *J. Chem. Soc., Perkin Trans. 2*, **1973**, 938.

5) Any spectral change was not detected in the photometric titration of **1** (7.0×10^{-6} mol dm^{-3}) with 2,6-lutidine up to 8.25×10^{-1} mol dm^{-3} in an acetonitrile solution. Other 2,6-disubstituted pyridines also gave the same results.

6) To a dry acetonitrile-benzonitrile solution (9:1 v/v) of **1** (1.25×10^{-4} mol dm^{-3}) and a base (0.125 mol dm^{-3}), hydrogen peroxide (6.4×10^{-2} mol dm^{-3}) in acetonitrile was added in a thermostated-reaction cell (10.0 ± 0.2 °C) equipped with a micro-oxygen electrode (YSI 5575).

7) T. C. Bruice and S. J. Benkovic, "Bioorganic Mechanisms," Vol. 1, W. A. Benjamin, New York (1966), p. 1.

8) The formation of the six-coordinated species of a manganese porphyrin with a nitrogen base shows the blue shift of Soret band in ≈10 nm. Photometric titration of **1**, however, with 1-methylimidazole showed the slight shift of the Soret band from λ_{max} = 467 to 468 nm. This evidenced the formation of only the corresponding five coordinated species. Selected formation constant K_1 (mol^{-1} dm^3) of the five-coordinated complex at 10.0 ± 0.2 °C; 1,5-Ph_2Im (137), 1,5-tBu_2Ph_2Im (904), Py (14.7), 3,4-Me_2Py (65.2), 1-MeIm (634), 4-Me_2NPy (1420).

9) I. Fita and M. G. Rossmann, *J. Mol. Biol.*, **185**, 21 (1985).

10) T. L. Poulos and J. Kraut, *J. Biol. Chem.*, **255**, 8199 (1980).

11) Abbreviations: 1-methylimidazole (1-MeIm), 1,5-diphenylimidazole (1,5-Ph_2Im), 1,5-(3,5-di-*t*-butylphenyl)imidazole [1.5-(3,5-tBu_2Ph)Im], pyridine (Py), 3-methylpyridine (3-MePy), 4-methylpyridine (4-MePy), 2,6-dimethylpyridine (2,6-Me_2Py), 3,4-dimethylpyridine (3,4-Me_2Py), 2,6-di-*t*-butylpyridine (2,6-tBu_2Py), 2,6-dimethylpyridine (2,6-Me_2Py), 2,6-dipheylpyridine (2,6-Ph_2Py), 2,4,6-collidine (2,4,6-Me_3Py), 4-methoxy-2,6-dimethylpyridine (4-MeO-2,6-Me_2-Py).

(Received September 27, 1994)