Evolution of Ethylene from 1-Aminocyclopropanecarboxylic Acid by Binuclear Iron(III)–Peroxide Adducts

Yuzo Nishida,*[a] Tetsuya Akamatsu,[a] Toshihiro Ishii[b] and Yoshiaki Oda[b]

[a] *Department of Chemistry, Faculty of Science, Yamagata University, Yamagata 990, Japan*
[b] *Department of Agricultural Chemistry, Faculty of Agriculture, Yamagata University, Tsuruoka 997, Japan*

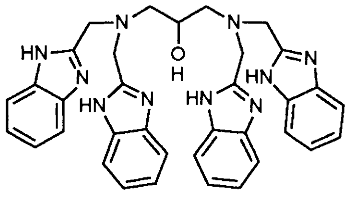
Significant ethylene evolution was observed in the reaction of 1-aminocyclopropanecarboxylic acid, binuclear iron(III) compounds and hydrogen peroxide; the origin of the ethylene is discussed in terms of the activation of peroxide ion by the binuclear iron(III) compounds.

Ethylene is a natural plant growth regulator involved in the control of a wide range of developmental responses: growth, abscission, senescence and fruit ripening to name but a few. Through the work of Adams and Yang,[1] and of Lurssen *et al.*,[2] the route for its formation from methionine *via* *S*-adenosylmethionine and 1-aminocyclopropanecarboxylic acid (ACC) seems well established.[3] However, the mechanism of the last step, namely the oxidation of ACC to ethylene, remains obscure. In order to elucidate the process in question, suitable synthetic model systems to produce ethylene are necessary. We have found that a significant amount of ethylene production occurs in reaction mixtures containing ACC, binuclear iron(III) compounds and hydrogen peroxide; we report here the origin of its production in terms of the activation of hydrogen peroxide by binuclear iron(III) compounds. As far as we know this is the first report on the ethylene evolution from ACC by a metal peroxide adduct.

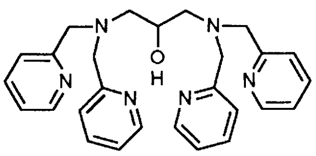
The binuclear iron(III) compounds used in this study are $[Fe_2(hptb)(OH)(NO_3)_2][NO_3]_2$,[4] and $[Fe_2(hptp)(OH)(NO_3)_2]\,[ClO_4]_2$.[5] In a typical run, the binuclear iron(III) complex (15 mg) and ACC (30 mg) were dissolved in 2.5 ml of water, and to this solution was added 2 ml of aqueous hydrogen peroxide (0.1 mol dm^{-3}); the vessel (total volume, 19 cm^3) was sealed with a butyl rubber cap. At appropriate times after mixing, 1 ml of the air in the head space was analysed by GC,† and results are shown in Fig. 1. As is known, mixtures of ACC and hydrogen peroxide give a small quantity of ethylene (*cf.* trace *C* in Fig. 1). The evolution of ethylene in the mixture with $[Fe_2(hptp)(OH)(NO_3)_2]^{2+}$ and hydrogen peroxide is remarkable, being much larger than that in the mixture containing $[Fe_2(hptb)(OH)(NO_3)_2]^{2+}$ and H_2O_2 (see *A* and *B* in Fig. 1). These facts indicate that the binuclear iron(III) complex–hydrogen peroxide system exhibits high ability for the evolution of ethylene from ACC, and also that its activity depends greatly on the complex used. No ethylene was detected in the absence of ACC under the same conditions.

---

† Conditions: glass column (d 3 mm; l 1.1 m); packing material, active alumina; carrier gas, N_2 (flow rate, 60 ml min^{-1}); column temperature, 80 °C; detector temperature, 90 °C; flame ionization detector.



Hhptb



Hhptp

It is known that the binuclear ion(III) compounds used in this study react with hydrogen peroxide to yield a 1 : 1 ratio peroxide adducts.[4,5] We have pointed out[6] that the peroxide ion trapped by binuclear iron(III) compounds is activated so that it has some degree of singlet oxygen ($^1\Delta_g$) character, and shows unique reactivity *via* its direct interaction with organic compounds such as alkenes,[7] DNA[8] and phenols.[9] The degree of activation of the peroxide ion depends on the complex used: activation by the hptp complex is much greater than that by the hptb complex, according to studies on the catalase- and bleomycin-like functions of these compounds.[5] Interestingly, the result obtained in this study, *i.e.* the activity of the complex with the hptp ligand for evolution of ethylene from ACC is much larger than that for the hptb complex, is in good accord with the previous results. Based on these discussions, it seems reasonable to assume that the evolution of ethylene observed in this study may proceed through the interaction between ACC and the activated peroxide ion trapped by the binuclear iron(III) compound.

In the methionine cycle in relation to ethylene biosynthesis, it has been proposed that the ethylene evolution occurs *via* the reaction between ACC and 'active oxygen species',[3] but the detailed nature of such species is not at all clear at present. The present work may provide an important key to elucidate the nature of the 'active oxygen species'.

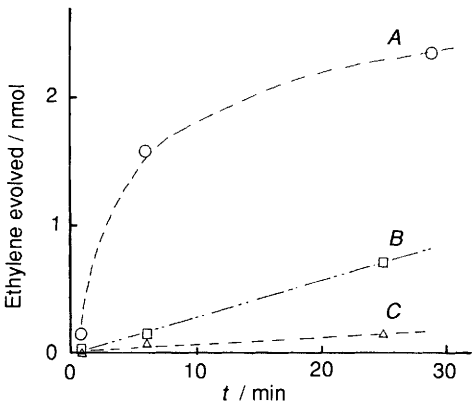


Fig. 1 Time dependence of ethylene evolution (see text). *A*: [Fe$_2$(hptp)(OH)(NO$_3$)$_2$]$^{2+}$; *B*: [Fe$_2$(hptb)(OH)(NO$_3$)$_2$]$^{2+}$; *C*: no iron complex.

Received, 27th November 1991; Com. 1/06028G

References

1 D. O. Adams and S. F. Yang, *Proc. Natl. Acad. Sci. USA*, 1979, **76**, 170.
2 K. Lurssen, K. Naumann and R. Schroder, *Z. Pflanzenphysiol.*, 1979, **92**, 285.
3 H. J. Miyazaki and S. F. Yang, *Physiol. Plantarum*, 1987, **69**, 366.
4 Y. Nishida, M. Takeuchi, H. Shimo and S. Kida, *Inorg. Chim. Acta*, 1985, **96**, 115; B. A. Brennan, Q. Chen, C. J. Garcia, A. E. True, C. J. O'Connor and L. Que, Jr., *Inorg. Chem.*, 1991, **30**, 1937.
5 Y. Nishida, M. Nasu and T. Akamatsu, *Z. Naturforsch.*, 1991, in the press.
6 Y. Nishida and M. Takeuchi, *Z. Naturforsch., Teil B*, 1987, **42**, 52; Y. Nishida and K. Takahashi, *J. Chem. Soc., Dalton Trans.*, 1988, 2003.
7 B. P. Murch, F. C. Bradley and L. Que, Jr., *J. Am. Chem. Soc.*, 1986, **108**, 5027.
8 Y. Nishida and T. Yokomizo, *Inorg. Chim. Acta*, 1989, **163**, 9.
9 Y. Nishida, T. Akamastu and M. Nasu, *Chem. Lett.*, 1991, 1703.