T-1312

# STUDIES OF CHEMICAL MODELING OF NITROGENASE CATALYSIS — NOVEL NITROGENASE INHIBITORS AND PROMOTERS AS CHEMICAL PROBES*

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In previous work from this laboratory, nitrogenase substrates of about a dozen known types were regarded as chemical probes, and multinuclear coordination activation of the exogenous substrates to cubane-like, or twin-cubanes-like cluster structural active-center was inferred[1, 2]. Recent publication of models of nitrogenase M-cluster and P-clusters by Rees *et al*, based upon single-crystal X-ray diffraction data with 2.7 Å resolution has shed new light on the structure of nitrogenase active-center[3]. In the present work, we aim to gain information from new chemical probes which alter the substrate specificities ($N_2$, acetylene, or proton reduction etc.) of nitrogenase, and believe that it will be very useful in examining and understanding the structure and function of the latest-proposed model of nitrogenase active center.

The behaviors of 1,2-bis(diphenylphosphino)ethane, a promoter of in vitro nitrogenase catalyzed acetylene reductive-hydrogenation, but an inhibitor of hydrogen-evolution reaction, as a new chemical probe of nitrogenase active center is reported, together with more detailed study on the behaviors of *o*-phthalaldehyde as a potent inhibitor of nitrogenase activity.

Tab. Effects of certain bidentate ligands on nitrogenase activity

| | *o*-Phthalaldehyde | $Ph_2PCH_2Ph_2$ | $Ph_2PCH_2CH_2Ph_2$ |
|---|---|---|---|
| $C_2H_2 \rightarrow C_2H_4$ | ↓ | ↘ | ↑ |
| $H_2$ evolution | ↓ | ↓ | ↓ |

The preliminary data we have acquired are consistent with the hypothesis of the two-sites model of $H_2$ evolution in nitrogenase MoFe-protein. Furthermore, in addition to the M-cluster, P-cluster is probably involved in the second site of $H_2$ evolution. Provided further information indicates that the functions of M- & P-clusters in nitrogenase catalysis to $N_2$ reduction reactivity may be different from that of acetylene reduction, for example, $N_2$ redution to $NH_3$ needs assistance of Mo, whereas acetylene reduction not.

References

[1] K. R. Tsai, H-B. Zhang, G-D. Lin, *Adv. in Sci. of China—Chemistry*, 1987, 2, 125.
[2] K. R. Tsai, H-L. Wan, H-T. Zhang, L-S. Xu, *The nitrogenase Fixation and its Research in China*, Springer-Verlag Berlin Heidelberg, 1992, 87.
[3] J. Kim and D. C. Rees, *Science*, 1992, 257, 1677.

* **This project is supported by a National Key Project of China.**