

Reduction of dinitrogen

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Conversion of dinitrogen to ammonia is required for all life. This conversion is accomplished by metalloenzymes on a scale of $\approx 10^8$ tons/year, a scale equivalent to that of the Haber–Bosch process (1) for making ammonia from dinitrogen and dihydrogen at high temperatures (350–550°C) and pressures [150–350 atmosphere (atm); 1 atm = 101.3 kPa]. Although the benefit of crop rotation has been known for centuries, not until 1930 was a metal (molybdenum) found to be required for efficient dinitrogen “fixation” in the soil (2), and not until the 1960s was it determined that an FeMo nitrogenase is responsible for fixation of dinitrogen (3–6). At approximately the same time (1965), the first dinitrogen complex (of Ru) was discovered by Allen and Senoff (7). In the 1960s, transition metals were beginning to reveal their prowess in catalytic transformations such as olefin hydrogenation. Therefore, a catalytic process for reducing dinitrogen at a low temperature and 1 atm appeared to be only a few years away. However, reduction of dinitrogen, probably the most stable diatomic known, by protons and electrons or by dihydrogen selectively to ammonia at room temperature and pressure proved to be much more difficult than anticipated.

The principles of reduction of dinitrogen to ammonia by Mo(0) and W(0) dinitrogen complexes were established in studies that began in the mid-1960s, primarily in the groups directed by Chatt and Hidai (8, 9). These studies demonstrated that dinitrogen could be bound and reduced to ammonia, apparently at a single metal center, but only one dinitrogen per metal and only stoichiometrically; catalytic reduction of dinitrogen to ammonia was never achieved.

The FeMo nitrogenase, which can be purified and crystallized, has been studied for decades. X-ray studies of the

FeMo nitrogenase carried out in the early 1990s revealed the now-well known $\text{Fe}_7\text{S}_9\text{Mo}$ core, where dinitrogen is likely to be reduced. This milestone naturally elicited a great deal of discussion concerning the mechanism of dinitrogen reduction. However, no definitive conclusions concerning the site and mechanism of dinitrogen reduction have yet been reached.

There are now two known catalytic reductions of dinitrogen under mild conditions. Both reductions require molybdenum. In the process reported by Shilov (10) in the early 1980s, dinitrogen is reduced to a mixture of hydrazine and ammonia ($\approx 10:1$). In the second process, reported by my group in 2003 (11), dinitrogen is reduced with protons and electrons to a mixture of ammonia and hydrogen in a ratio approximately the same as that found in FeMo nitrogenase (one hydrogen per dinitrogen reduced). Although the turnover number in the second system is low (≈ 4 equivalents of dinitrogen are consumed), the conclusion that reduction takes place at a single Mo center through intermediates of the type proposed originally by Chatt and his group (8) seems inescapable.

The possibility that an efficient “non-biological nitrogenase” can be perfected in the long run cannot be dismissed lightly, even though the huge and highly successful Haber–Bosch process is unlikely to be displaced readily by a new process, even if that new process were efficient and inexpensive. However, it must be kept in mind in these days of energy concerns that $>1\%$ of the energy consumed by humans is consumed by the Haber–Bosch process.

Interest in dinitrogen reduction is being revived to some degree today, primarily because this reaction will always be required for life as we know it, because we now know that it is possible to reduce dinitrogen catalytically with pro-

tons and electrons at a single molybdenum center, and because the intellectual challenges for inorganic, bioinorganic, and biological chemists in understanding dinitrogen reduction are as great as they have ever been. Are there many ways to reduce dinitrogen to ammonia under mild conditions? Are all nitrogenases structurally and functionally closely related? Is molybdenum the most efficient metal for dinitrogen reduction? Is it possible to form products from dinitrogen that contain a nitrogen–carbon bond? Contributions that search for answers to these and other important questions both from the biological and the inorganic perspectives can be found in this special feature in this issue.

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