The Protonation of Bridging Dinitrogen to yield Ammonia

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The protonation of the V^{II} bridging dinitrogen complex $[\{V(C_6H_4CH_2NMe_2)_2(C_5H_5N)\}_2N_2]$ yields $2/3NH_3$, $2/3N_2$ and unidentified V^{III}-containing products, although hydrazine might have been expected on the basis of its structure; another factor influencing the product of dinitrogen protonation appears to be the availability of electrons from the metal atoms.

The protonation of dinitrogen terminally bound at one end only to elements such as molybdenum has been extensively studied preparatively[1] and kinetically,[2] and the mechanism of protonation to yield ammonia has been fitted to the kinetics of the reduction of dinitrogen by molybdenum-containing nitrogenases.[3] The parallels between chemical and biochemical studies are persuasive, even granting that molybdenum(0) [and even more vanadium (−I)][4] are oxidation states unlikely to be achieved in enzyme systems. In contrast, the protonation of bridging dinitrogen has no obvious parallel with biological processes, and has been generally believed to lead to hydrazine.[5]

We have now shown that the bridging dinitrogen in the first stable dinitrogen complex of vanadium, $[\{V(C_6H_4CH_2NMe_2)_2(C_5H_5N)\}_2(\mu\text{-}N_2)]$,[6] which contains a linear VNNV system with V–N = 1.833(3) Å and N–N = 1.228(4) Å,[6] gives a stoichiometric yield of ammonia, based upon 2 electrons being used for the reduction and no hydrazine or dihydrogen upon protonation with HCl, the vanadium atoms changing oxidation state from II to III. In fact, if $[VCl_2(tmeda)_2]$ (tmeda = tetramethylethylenediamine) is mixed with $LiC_6H_4CH_2NMe_2$, dinitrogen uptake is rapid up to a maximum of 1 N_2 per 2 vanadium atoms, but whatever the ultimate dinitrogen uptake, one third of it is converted to ammonia upon acid treatment. Pyridine is apparently necessary only to cause crystallisation of a dinitrogen complex.

We have so far not prepared $^{15}N_2$ derivatives. However, treatment of $[VCl_2(tmeda)_2]$ with acid yields only a trace of ammonia, and mixing $[VCl_2(tmeda)_2]$ with $LiC_6H_4CH_2NMe_2$ under Ar followed by protonation yielded no ammonia or hydrazine. We showed by titration that the ultimate vanadium-containing product is vanadium(III). In normal practice we determined ammonia by base distillation after protonation. However, we also showed that ammonia was present in the reaction mixture after protonation but before distillation, though an accurate quantitative determination was not achieved in the reaction mixture. Hydrazine appears not to be an intermediate in the protonation reactions because addition of hydrazine to the dinitrogen complex before protonation caused no increase in ammonia yield (a decrease was actually observed) and the recovery of hydrazine was *ca.* 85%. The yield of ammonia was not increased by adding zinc amalgam as a reductant to the dinitrogen complex.

All our data, including a complete dinitrogen balance, fit eqn. (1).

$$2V^{II} + N_2 + 2H^+ \rightarrow 2/3NH_3 + 2/3N_2 + 2V^{III} \qquad (1)$$

The reduction of a bridging N_2 ligand to ammonia in this

Table 1 Protonations and structures of bridging dinitrogen complexes

	M–N–N/°		N–N/Å	Acid	Protonation products, yield[a]	Ref.
$[\{Mo(C_5Me_5)Me_3\}_2(N_2)]$	172.0(2)	176.7(2)	1.236(3)	HCl	NH_3(16%)	7
$[\{W(C_5Me_5)Me_3\}_2(N_2)]$	167.0(16)	170.2(16)	1.334(26)	HCl	NH_3 (16%) $[\{W(C_5Me_5)(Me_2Cl)\}_2(N_2)]$	7,10
$[\{Zr(C_5Me_5)_2N_2\}_2(N_2)]$	176.7(3)	177.4(3)	1.182(5)[b]	HCl	N_2H_4 (33%) N_2(67%) $[Zr(C_5Me_5)_2Cl_2]$	11
$[\{Nb(S_2CNEt_2)_3\}_2(N_2)]$	166.8(9)	163.1(9)	1.252(16)	HCl	N_2H_4 (100%) $[Nb(S_2CNEt_2)_3Cl_2]$	12
$[\{Ta(S_2CNEt_2)_3\}_2(N_2)]$	—	—	—	HCl	N_2H_4 (100%) $[Ta(S_2CNEt_2)_3Cl_2]$	12
$[\{V(C_6H_4CH_2NMe_2\text{-}2)_2(C_5H_5N)\}_2(N_2)]$	171.6(3)	171.3(3)	1.228(4)	HCl	NH_3 (33%) N_2 (67%) V^{III}	

[a] Based on total N_2 content. [b] Bridging dinitrogen.

vanadium system contrasts with its reduction to hydrazine in other complexes (see Table 1 for some examples). The sole additional exceptions are $[\{M(C_5Me_5)Me_3\}_2N_2]$[7,10] (M = Mo or W) which yield some ammonia but apparently not corresponding to any obvious stoichiometry. The data now available suggest that the bridging dinitrogen structure does not uniquely determine the product of protonation even where a formal representation based on X-ray structure analysis might require a reduced form of dinitrogen (N_2^{2-} or N_2^{4-}). The number of electrons available must also be important, and if there are less than four then ammonia apparently can be produced directly, and not necessarily *via* hydrazine. In these circumstances, it is unwise to exclude consideration of bridging dinitrogen in the chemistry of nitrogenases. Our data are also in accord with the initial steps postulated in Shilov's mechanism for the reduction of dinitrogen (bridging N_2, $V^{II} \rightarrow V^{III}$)[8] rather than Schrauzer's (side on N_2, $V^{II} \rightarrow V^{IV}$)[9] though we do not require N_2H_4 as an intermediate as both these suggestions do.

We are currently attempting to clarify the detailed mechanisms of protonation of bridging dinitrogen in vanadium systems.

This work was supported by EEC Research Grant ST2*410 (to R. P.-A.).

Received, 8th May 1991; Com. 1/02181H

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