

ACCOUNTS OF CHEMICAL RESEARCH®

APRIL 1992

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Protonation of Coordinated Dinitrogen

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Received September 3, 1991

The first dinitrogen complex, $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$, was identified in 1965 by Allen and Senoff,¹ who were attempting to obtain $[\text{Ru}(\text{NH}_3)_6]^{2+}$ using a method of preparation which had been published some 20 years earlier.² This makes it very likely that it was synthesized unknowingly considerably earlier than 1965, but the discovery was certainly greeted with considerable acclaim. It had been foreseen in many circles, in part because of the isoelectronic nature of carbon monoxide and dinitrogen, and in part because it was known that microorganisms could convert dinitrogen to ammonia, and that this transformation is metal-dependent (molybdenum- and/or vanadium-dependent).³ It was a simple matter to postulate initial metal-dinitrogen binding in these biological systems.⁴

The discovery of $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$, together with the announcement of some less-well-characterized systems for fixing nitrogen uncovered by Vol'pin and his co-workers in Moscow,⁵ encouraged a huge amount of research into dinitrogen complexes and their reactions. The fears of some of us (who were privileged to be paid to do this kind of research) that $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ would provide a facile route from dinitrogen to ammonia and force us to seek alternative employment were confounded. Despite the steady stream of new dinitrogen complexes,⁶ it was not until 1972 that the first reaction of coordinated dinitrogen to give a well-defined complex product was announced.⁷ This was an acetylation and was followed shortly by the discovery of the protonation of coordinated dinitrogen to give hydrazido(2-) complexes and the subsequent conversion

of this intermediate species to ammonia.⁸ Despite all this, it is only now that patterns of reactivity and mechanism are beginning to emerge. This Account attempts to assess the data at hand at present.

Dinitrogen Complexes

By far the largest single class of dinitrogen complex has end-on coordinated dinitrogen, singly bound. Stable compounds with as many as three dinitrogens per metal atom, as in $[\text{Mo}(\text{N}_2)_3(\text{PPr}^n\text{Ph})_3]$, are known.⁹ All the structural studies indicate that the N-N bond length is ca. 1.12 Å, and no obvious relation of N-N length with structure or reactivity has emerged among the many dinitrogen complexes of this class now known. A distance of 1.12 Å represents a minor lengthening of the N-N bond compared to free dinitrogen (1.0968 Å)¹⁰ and cannot in any way be construed as an indication of "activation". The metal-nitrogen bonds are generally believed to be multiple, with σ - and π -components very much like the classical picture for the binding of carbon monoxide (Figure 1).

Complexes of iron show N-N bond lengths very similar to those of vanadium, though their reactivities are very different. It has been assumed that $\nu(\text{NN})$, which is generally infrared active in these compounds, will be a measure of the strength of metal-dinitrogen binding because a low value of $\nu(\text{NN})$ suggests metal $d\pi$ donation into the N-N antibonding system. In addition (see

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G. Jeffery Leigh was born in London, England, in 1934. He performed his undergraduate and graduate work at King's College, University of London, and in 1959 became a lecturer in the University of Manchester. He took a sabbatical year in Munich with E. O. Fischer in 1963, and this turned his interest to transition metal chemistry. In 1965 he joined the recently established Nitrogen Fixation Unit at the University of Sussex, where he has been ever since, currently as Deputy Head of Laboratory. His principal research interest is chemical and biological nitrogen fixation, but he also has interests in organometallic chemistry.

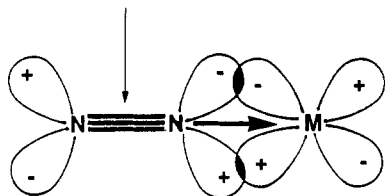


Figure 1. The N_2 molecule donates a lone pair of electrons to the metal atom and receives π -electrons in return from metal d orbitals into its π -antibonding orbitals. Note that on symmetry grounds a similar interaction with a metal is feasible along the axis represented by the vertical arrow (side-on bonding).

below), a low value of $\nu(NN)$ should be indicative of activation to protonation since it should imply negative charge buildup on the dinitrogen. Consequently, activation and strong metal–dinitrogen binding might be expected to go together and be indicated by low values of $\nu(NN)$. It is therefore not obvious why $[FeH(N_2)(dmpe)_2]^+$ ($dmpe = Me_2PCH_2CH_2PMe_2$, $\nu(NN) = 2094\text{ cm}^{-1}$),¹¹ should have a nonactivated and relatively nonlabile dinitrogen, whereas *trans*- $[V(N_2)_2(dmpe)_2]^-$ has an exceedingly low value of $\nu(NN)$, 1763 cm^{-1} , and as expected, an activated dinitrogen, which can, however, be easily pumped away at room temperature.¹² The theory is not entirely adequate to explain this.

The second most numerous class of dinitrogen complexes contains bridging dinitrogen. In the symmetrical linear case, the most usual, the NN stretching vibration is not IR active, though it is of course Raman active. Consequently, there is less information available as to $\nu(NN)$. The N–N separations tend to be larger than in the terminally-bound case, but vary from 1.12 Å to about 1.3 Å. Formally one can envisage the dinitrogen moiety as neutral dinitrogen at one extreme, $(N_2)^{2-}$ at an intermediate length, and $(N_2)^{4-}$, i.e., a hydrazine derivative, at the other. Often it is a matter of fancy which formulation one adopts. For example, $[V(C_6H_4CH_2NMe_2)_2(C_5H_5N)_2N_2]$ has magnetic properties consistent with V^{II} , but an N–N separation of ca. 1.23 Å, suggestive of an N–N double bond, and hence V^{III} .¹³ There are other kinds of binding, side-on as in $[Sm(C_5Me_5)_2]_2N_2$ ¹⁴ and simultaneously side-on and end-on as in $K[Co(N_2)(PMe_3)_3]$,¹⁵ but these are relatively rare, often contain very “stretched” dinitrogen molecules $[(N_2)^{4-}]$, and usually contain activated dinitrogen. The protonation reactions have not been fully reported for even the few cases which are current, and they show no obvious pattern as yet. They will not be discussed further here.

Reactivity of Singly Bound End-On Dinitrogen

The first reaction of a coordinated dinitrogen to give a completely characterized dinitrogen-containing complex product is that shown in reaction 1.⁷ We inter-

$$[W(N_2)_2(dppe)_2] + CH_3COCl \rightarrow [WCl(N_2COCH_3)(dppe)_2] + N_2 \quad (1)$$

$dppe = Ph_2PCH_2CH_2PPh_2$

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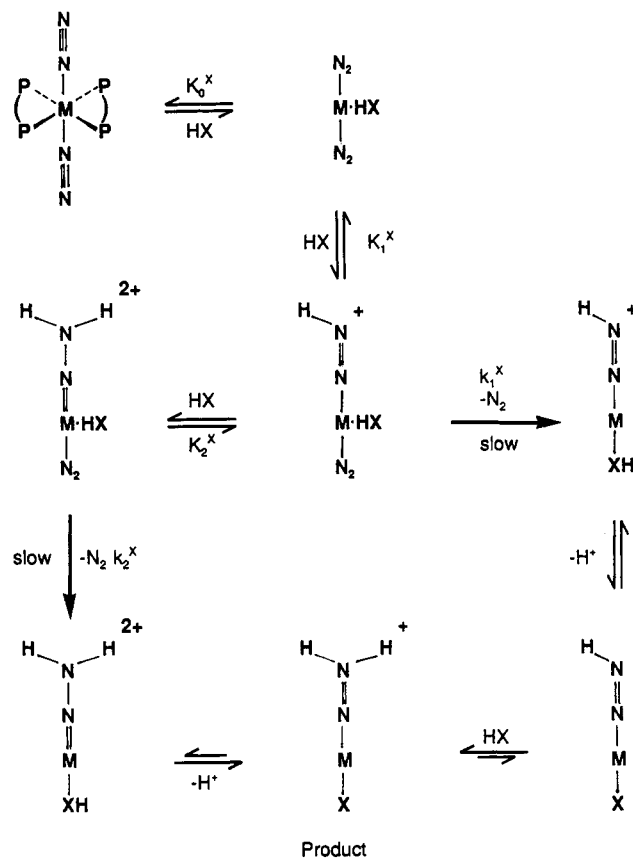


Figure 2. The mechanism of protonation of end-on singly-bound coordinated dinitrogen in molybdenum(0) and tungsten(0) complexes by acids in tetrahydrofuran.¹⁷ Note that the diphosphine, $Ph_2PCH_2CH_2PPh_2$, is omitted in all representations except the first.

preted this reaction as being essentially an oxidative addition to a $WN\equiv N$ fragment, with the principal step being nucleophilic attack of the coordinated N_2 on the carbon of the acetyl group. Subsequently, this work was extended to protonation reactions,⁸ and even to alkylation reactions, which, however, generally proceed via attack of an alkyl radical R^\bullet , generated by homolysis of an alkyl halide, upon dinitrogen.¹⁶ The mechanism of the protonations, at least in the initial stages as far as the $=NNH_2$ stage, was established by kinetic studies and is shown in Figure 2.¹⁷ In circumstances where some ligands are labile, as in $[W(N_2)_2(PMe_2Ph)_4]$, but not in $[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$, the protonation may be carried through to ammonia. Even where no ligands are labile, the reduction may be carried through to ammonia if additional electrons are supplied chemically¹⁸ or electrochemically.¹⁹ In the latter case, a genuine cyclic process has been evolved.

Figure 3 shows the pattern of N_2 complex formation and of activation to protonation of dinitrogen complexes. The vertical line shows the boundary between those complexes in reasonably accessible oxidation states with dinitrogen which react with acids, and those which do not produce hydrazine and/or ammonia upon addition of acid. The elements which activate di-

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Sc ^G	Ti ^{A,B?}	V ^A	Cr ^F	Mn ^F	Fe ^{A,D}	Co ^D	Ni ^D
Y ^G	Zr ^{A,B?,C}	Nb ^B	Mo ^{A,B,E}	Tc ^F	Ru ^F	Rh ^F	Pd ^G
La ^C	Hf	Ta ^B	W ^{A,B,E}	Re ^D	Os ^F	Ir ^F	Pt ^G

Figure 3. Binding of dinitrogen and its activation toward protonation. A: Terminal, end-bound N_2 activated to protonation, yielding ammonia and/or hydrazine. B: Bridging, end-bound N_2 activated to protonation. In some cases (represented by B?) it is not clear whether bridging or terminal dinitrogen (or both) is activated. C: Side-on N_2 activated to protonation. Sm is the unique example to date among the lanthanoids and lanthanum. D: Other activated N_2 . In these systems additional reductant is required. For Re, acetylation, but not protonation, has been observed. E: Terminal, end-bound N_2 activated to alkylation, yielding diazenido complexes. F: N_2 complexes reported, but no evidence suggesting N reactivity. G: No N_2 complexes stable at 20 °C unambiguously characterized.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni
6.54	6.82	6.74	6.77	7.44	7.87	7.86	7.64
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
6.38	6.84	6.88	7.10	7.28	7.37	7.46	8.34
La	Hf	Ta	W	Re	Os	Ir	Pt
5.88	6.65	7.89	7.98	7.88	8.7	9.1	9.0

Figure 4. First ionization energies (eV) of some transition elements for the reaction $M(g) \rightarrow M^+(g) + e$.

nitrogen are primarily those of transition metal groups 4–6 of the periodic table.

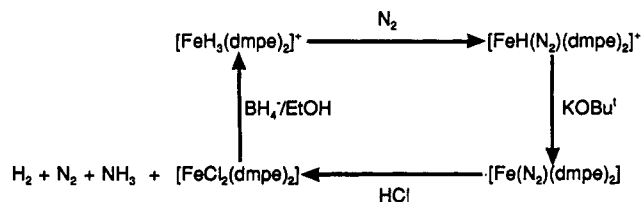
Why this should be can be explained reasonably satisfactorily. If we are dealing with nucleophilic attack by coordinated dinitrogen on protons, those dinitrogens with the higher negative charge provided by the metal–dinitrogen π -donation into the N_2 antibonding orbitals should be the more effective. The first ionization potentials of the elements can give us an indication of how easy the release of electrons from a metal into coordinated dinitrogen might be. Thus, for the reaction $M \rightarrow M^+ + e$, the energy rises from 6.54 at Sc to 6.77 at Cr and 7.44 at Mn (all in electronvolts) and remains above 7.5 V thereafter. Successive ionization energies show the same pattern. This is shown in Figure 4 for most of the transition elements. Of course, to make comparisons simply on the basis of observed reactivity in a diverse selection of compounds with different oxidation levels, stoichiometries, and structure and expect correlation with a single parameter such as ionization potential is not reasonable. We do not have enough dinitrogen compounds of different elements which are strictly comparable (e.g., $[V(N_2)_2(dmpe)_2]^-$, $[Mo(N_2)_2(dppe)_2]$) to be able to make the detailed comparisons one would wish for. However, at least within a period, it is apparent that those elements which ionize the more easily are also those which activate dinitrogen to protonation.

This rationale is obviously very superficial. For example, we do not yet understand, and the analysis cannot explain, why the yields and products (ammonia and/or hydrazine) from the protonation of $[Mo(N_2)_2-$

$(PMe_2Ph)_4]$ change with acid and with solvent.

As long as all nitrogenases were believed to be of a similar kind, namely, with molybdenum supposedly at the active site, the chemistry of dinitrogen as exhibited in complexes of transition metals of group 6 was believed in many circles to exemplify the kind of chemistry used by nitrogenase. The discovery of a vanadium–iron nitrogenase entailed some adjustment of views, there being a rather limited vanadium dinitrogen chemistry. The recognition of a third kind of nitrogenase,²⁰ containing iron as the only metal species, posed the question, how is it possible to convert dinitrogen to ammonia on iron, when theory and practice suggest that this should require very high degrees of reduction of iron, perhaps into negative oxidation states? Until recently, chemistry seemed to imply that conditions very far removed from those pertaining to biological systems might be obligatory. We can employ strong reducing agents to produce very reactive, reduced species which can pick up dinitrogen and then be protonated. An example is the species $Li_2[Fe(C_{10}H_7)_4] \cdot 2Et_2O$ of tetrahedral structure, which can be reduced with LiPr to yield a species which picks up N_2 and gives hydrazone upon acid solvolysis. The active species may be related to the characterized nitrogen-fixing species $Li_4[FePh_4]$.²¹ Such complexes are of inherent interest, but do not seem to provide realistic models for nitrogenase function.

These systems may be distinct from those containing a transition metal compound and a nonaqueous reducing agent, such as $FeCl_3/LiPh$. There is no hard evidence of mechanism in most of them. It is likely that many involve nitridation of dispersed metal formed by strong reduction and that N–N bond splitting occurs before the acid hydrolysis produces ammonia. However, very recently it has been shown that a formally iron(0) dinitrogen complex can be reached simply by adding base to an iron(II) dinitrogen complex.²² This is sketched out below. The iron(0) dinitrogen complex $[Fe(N_2)(dmpe)_2]$ has a relatively high value of $\nu(N_2)$ (1975 cm^{-1}) and reacts with acids, when there is then apparently a choice of protonation sites, the iron atom or the dinitrogen. When the iron is protonated, N_2 and H_2 are generated. When the dinitrogen is protonated, the ultimate product is apparently ammonia. Currently our best yields are ca. 18% though the mechanism of the formation of ammonia is completely obscure at present. Reference to Figure 3 suggests that ruthenium might be an even better bet for this kind of reaction, but clearly more than simple consideration of ionization energies is required to develop a general theory of dinitrogen activation.



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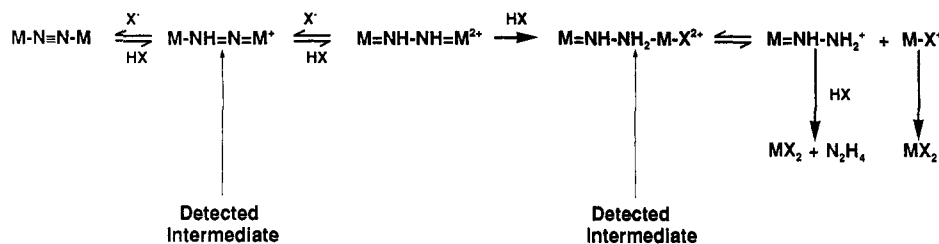


Figure 5. Mechanism of the protonation of bridging dinitrogen in $[\{M(S_2CNET_2)_3\}_2N_2]$ ($M = Nb$ or Ta), after Henderson.²⁷

Table I.
Protonations^a and Structures of Bridging Dinitrogen Complexes

	MNN/deg	N-N/Å	products (yields) ^b	ref
$[\{Mo(C_5Me_5)_2Me_3\}_2N_2]$	172.0 (2), 176.7 (2)	1.236 (3)	NH_3 (16%)	(Schrock) ²⁸
$[\{W(C_5Me_5)_2Me_3\}_2N_2]$	167.0 (16), 170.2 (16)	1.334 (26)	$[\{W(C_5Me_5)_2Me_2Cl\}_2N_2]$	(Schrock) ²⁸
$[\{Zr(C_5Me_5)_2N_2\}_2N_2]$	176.7 (3), 177.4 (3)	1.182 (5)	N_2 (67%), N_2H_4 (33%), $[Zr(C_5Me_5)_2Cl_2]$	(Bercaw) ³¹
$[\{Nb(S_2CNET_2)_3\}_2N_2]$	166.8 (9), 163.1 (9)	1.252 (16)	N_2H_4 (100%), $[Nb(S_2CNET_2)_3Cl_2]$	(Henderson) ²⁷
$[\{Ta(S_2CNET_2)_3\}_2N_2]$			N_2H_4 (100%), $[Ta(S_2CNET_2)_3Cl_2]$	(Henderson) ²⁷
$[\{V(C_6H_4CH_2NMe_2)_2(C_6H_5N)\}_2N_2]$	171.6 (3), 171.3 (3)	1.228 (4)	NH_3 (33%), N_2 (67%), V^{III}	(Leigh) ²⁹

^aWith HCl. ^bBased on total N_2 content.

Special Case of Bridging Dinitrogen Complexes

We consider here simple bridging compounds of the form $M-N_2-M$. Many of these have now been described, the majority with both M atoms of the same metal, others, but fewer, with M atoms that are different. They all seem to have linear $M-N-N-M$ systems, but the $N-N$ bond lengths cover a considerable range, always larger than in free N_2 . This is interpreted as meaning that the metal atoms are already beginning the reduction of the dinitrogen.

Bridging dinitrogen complexes are also important for other reasons. Several proposals have been made to the effect that bridging dinitrogen, perhaps in the moiety $Fe-N_2-Mo$, is important in nitrogenase function. Alternatively, a considerable number of aqueous dinitrogen-fixing systems are known. The most important from the point of view of this discussion are those based on vanadium. Although the key intermediates have not been isolated and characterized in the usual sense, there has been a wide range of kinetic studies which have been interpreted in terms of a mechanism. Thus, in two rather different systems, $V(OH)_2/Mg(OH)_2/KOH$, a solid gel which converts dinitrogen to ammonia and hydrazine,²³ and $V^{II}/C_6H_4(OH)_2-1,2$, which catalytically reduces dinitrogen to ammonia in the pH range 9–11,²⁴ the key intermediates have been suggested to contain dinitrogen bridging between two V^{II} atoms, themselves part of dinuclear clusters in the gel system or of a polynuclear catechol–vanadium chain species in the second case. In both cases, reduction of dinitrogen by four electrons to give N_2H_4 has been postulated, any ammonia arising by subsequent reduction of hydrazine by more vanadium(II). In these reductions, vanadium(II) is oxidized to vanadium(III).

It should be noted that for the gel systems an alternative mechanistic interpretation has been advanced, involving side-on binding to a single vanadium(II) (for which there is little precedent in model compounds), production successively of diazene and hydrazine, and oxidation of vanadium(II) to vanadium(IV).²⁵ Whether

this mechanism is valid is a matter of considerable disagreement. It has also been claimed for some related molybdenum systems.²⁶

The protonation of bridging dinitrogen in the complexes $[\{M(S_2CNET_2)_3\}_2N_2]$ ($M = Nb$ or Ta) has been studied kinetically by Henderson.²⁷ The production of hydrazine from these complexes by HCl results in the formation of $[M(S_2CNET_2)_3Cl_2]$ ($M^{III} \rightarrow M^V$). The mechanism proposed is shown in Figure 5.

This observation of hydrazine in these systems lends credence to the idea, reinforced by some of the selected data shown in Table I, that hydrazine (or possibly diazene) is the likely product of protonation of bridging dinitrogen. Most recent results suggest that this is not necessarily the case.

In a recent paper, Schrock²⁸ has described how the protonation of $[\{Mo(C_5Me_5)_2Me_3\}_2N_2]$ ($N-N = 1.236$ (3) Å) with HCl gives rise to ammonia derived from 16% of the coordinated N_2 , and no hydrazine. No other products have been identified. This corresponds to about one electron used per two Mo atoms or per dinitrogen molecule. Yields are higher if a subsidiary reducing agent is present, but this introduces a complication which we shall not consider here. Apparently, the tungsten analogue yields $[\{W(C_5Me_5)_2Me_2Cl\}_2N_2]$ ($N-N = 1.334$ (26) Å) and also ca. 16% ammonia in similar conditions.

The vanadium(II) dinitrogen bridging complex $[\{V(C_6H_4CH_2NMe_2)_2(C_6H_5N)\}_2N_2]$ ($N-N = 1.228$ (4) Å) with HCl produces $2/3 NH_3$, $2/3 N_2$, no N_2H_4 , no H_2 , and what are certainly V^{III} -containing products,²⁹ though they have yet to be characterized. Other experimental data make it clear that the dinitrogen is the source of the ammonia and that hydrazine is not an intermediate. Consequently, it is evident that ammonia can be a direct product of the protonation of bridging dinitrogen. In this context, it should be noted that the vanadium–iron nitrogenase produces a little hydrazine from N_2 ,

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as well as ammonia, whereas the molybdenum-iron nitrogenase produces only ammonia.³⁰

Conclusions

These results cannot be explained simply, but some generalizations can be made. First, there is a general rule about ease of release of electrons from a metal atom correlating with activation of dinitrogen to protonation. This holds both for end-on singly-bound dinitrogen and for bridging dinitrogen, but it is not sufficient to explain all the observations. It applies only to the first step of the protonation reaction, which can lead either to ammonia or to hydrazine. Second, for conversion to ammonia six electrons are necessary for a stoichiometric reaction, but ammonia can still be produced if fewer are available. For example, with singly-bound end-on N_2 as in $[V(N_2)_2(dmpe)_2]^-$, reaction with HCl gives approximately $\frac{4}{3}NH_3$ and four electrons are involved ($V^{-I} \rightarrow V^{III}$).¹² Thus four electrons do not invariably produce hydrazine. Third, if fewer than four electrons are available in the system, then protonation of end-on N_2 cannot give the formal $M^{IV}=\text{NNH}_2$ intermediate from $M^0 \leftarrow N_2$, because this requires four electrons. However, if the intermediate were to be more accurately described by $M \leftarrow N^-=N^+H_2$ (an isodiazene complex), then this might be attainable with only two electrons used. Examples of isodiazene complexes are rare. Protonation of bridging dinitrogen when fewer than four electrons are available apparently also leads preferentially to ammonia rather than hydrazine.

The availability of electrons from a metal atom is clearly an expression of the redox potential exhibited for the oxidation states selected and in the specific ligand environment. However, for none of the fixing systems we have discussed are meaningful redox potentials available. Nevertheless, it is not unexpected, thinking, for example, of the group V dinitrogen complexes, that niobium and tantalum reach higher oxidation states than does vanadium under comparable conditions. In general, the best we can do is to look at data for a standard set of conditions, and these do indeed reveal some interesting features.

Figure 6 shows some oxidation potentials for a series of couples which are of interest in the present context. They refer to aqueous solution at unit activity for the hydrogen ion. The convention used is such that couples lower (more negative) should be capable of reducing couples higher (more positive). The data are taken directly from, or interpolated from, ref 32. The data

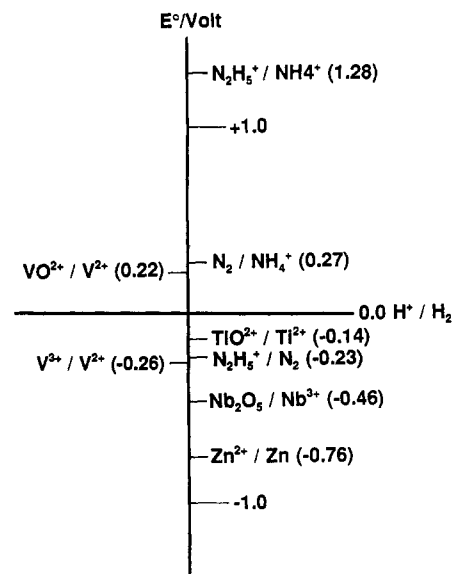


Figure 6. Redox potentials for selected systems in acid solution ($a_H = 1$).

suggest that Zn should be capable of producing both hydrazine and ammonia from dinitrogen in aqueous acid solution. To date we have no indication that it can. The Nb_2O_5/Nb^{3+} couple should be able to do the same. In fact, only hydrazine has been observed. The TiO^{2+}/Ti^{2+} couple also produces hydrazine, though these data suggest that it is about 0.1 V too positive. The most interesting observation is that VO^{2+}/V^{2+} is nearly 0.5 V too positive to produce hydrazine and has nearly the same potential as N_2/NH_4^+ . However, V^{3+}/V^{2+} should be well able to reduce dinitrogen to ammonia, but the reaction to give hydrazine is much more evenly balanced. This is happily consistent with the observations of ourselves and others in vanadium systems where V^{III} is claimed to be the oxidation state resulting from dinitrogen protonations. Whether any other predictions made with such data will turn out to be justified remains to be proven.

These considerations indicate only what is thermodynamically feasible and give no information about kinetic factors. It may happen that the pathway less favored thermodynamically is kinetically the more facile. Much more mechanistic work on well-defined dinitrogen protonation systems is clearly called for.

Our current data suggest that the availability of four electrons may produce hydrazine and will certainly do so in bridging dinitrogen compounds. Fewer or more than four electrons will probably give ammonia whether the dinitrogen is singly bound or bridging. The N-N separation in the complexes as well as, by extension, $\nu(N_2)$ is a guide neither to activation to protonation nor to the eventual product.

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