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The Reduction of Molecular Nitrogen, Organic Substrates, and Protons by Vanadium(II)¹

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Abstract: The reaction of molecular nitrogen with alkaline suspensions of $\text{V}(\text{OH})_2$ in $\text{Mg}(\text{OH})_2$ is shown to yield hydrazine via diimide, N_2H_2 , as the intermediate. The yields of hydrazine depend critically on the $\text{V}^{2+}/\text{Mg}^{2+}$ ratio in the hydroxide gels. At higher than optimal V^{2+} concentrations the yields of N_2H_4 decline and hydrogen is evolved instead. Coprecipitation of $\text{V}(\text{OH})_2$ with $\text{ZrO}_2\cdot\text{aq}$ also produces gels which also reduce nitrogen to hydrazine, although less efficiently than $\text{V}(\text{OH})_2$ - $\text{Mg}(\text{OH})_2$ systems. In the absence of a host lattice, only traces of hydrazine are formed by the reaction of nitrogen with $\text{V}(\text{OH})_2$ while hydrogen production occurs to a greater extent. The reduction of acetylene to ethylene, or of ethylene to ethane by $\text{V}(\text{OH})_2$ does not require a host lattice. Studies of the reaction stoichiometries reveal that $\text{V}(\text{OH})_2$ acts as a two-electron reductant. Reduction of acetylene, ethylene, and, to a slight extent, of nitrogen was also found to occur in acidic solutions of V^{2+} (aq) on irradiation with uv light.

In part 1 of this series we reported on the evolution of H_2 from suspensions of $\text{Fe}(\text{OH})_2$ and also described the reduction of a number of organic substrates as well as of molecular nitrogen.² We subsequently directed our attention to the reactions of $\text{V}(\text{OH})_2$, a powerful reducing agent, which is known to undergo spontaneous decomposition with H_2 evolution.³ Moreover, Shilov et al.^{4,5} demonstrated that $\text{V}(\text{OH})_2$, coprecipitated with $\text{Mg}(\text{OH})_2$, reduces not only C_2H_2 to C_2H_4 , but also N_2 to N_2H_4 . The latter reaction has been the subject of extensive investigations, but its mechanism is as yet unknown.

It has been suggested⁶ that V^{2+} acts as a one-electron reductant and that its incorporation into the $\text{Mg}(\text{OH})_2$ lattice favors an aggregation of four V^{2+} ions. These "quadrupoles" were assumed to reduce N_2 directly to N_2H_4 . A reaction of such high order should have very low statistical probability and is experimentally not well supported. Recent studies⁷ with isotopically labeled N_2 revealed that the original N-N bond of the substrate remains intact during its reduction to N_2H_4 . Attempts to detect the intermediacy of diimide, N_2H_2 , did not produce conclusive results.⁷ Since N_2H_2 has been shown to be

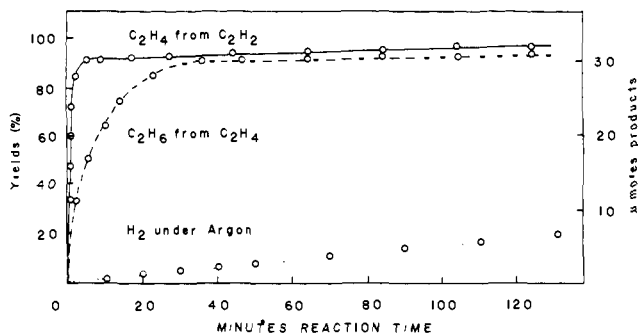


Figure 1. Reduction of C_2H_2 and of C_2H_4 by $V(OH)_2$ - $Mg(OH)_2$ in 8 N KOH at 25 °C as a function of time, compared to H_2 evolution in the same system under argon. The substrates C_2H_2 and C_2H_4 were initially present at 1 atm. The gels consisted of 2000 μmol of $Mg(OH)_2$ coprecipitated with 35 μmol of $V(OH)_2$.

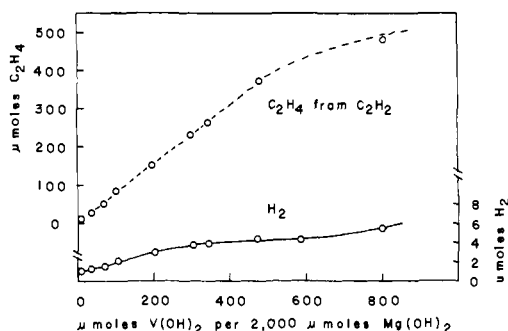


Figure 2. Reduction of C_2H_2 and H_2 evolution as a function of the V^{2+} content of $Mg(OH)_2$. Yields of product were determined after 90 min of reaction at 25 °C and the initial pressure of C_2H_2 of 1 atm. The amount of $Mg(OH)_2$ was 2000 μmol in all cases.

the initial product of N_2 reduction in nitrogenase model systems,^{8,9} we decided to reinvestigate the reduction of N_2 by vanadous hydroxide. Since the reactions of $Fe(OH)_2$ are stimulated by uv light,² we also investigated the effect of light on the reactions of $V(OH)_2$. Although the results of these experiments were negative, we in turn discovered that the evolution of H_2 as well as the reduction of certain substrates by V^{2+} (aq) in homogeneous acidic solutions is uv-light stimulated. Initial results of this work will be described. However, the main thrust of the present paper is directed toward the elucidation of the mechanism of N_2 reduction in alkaline $V(OH)_2$ - $Mg(OH)_2$ systems. The reduction of C_2H_2 , of 2-butyne, and of C_2H_4 and the formation of H_2 were investigated as well, as these reactions provide the basis for the understanding of the mechanism of N_2 reduction.

Results

Reduction of C_2H_2 , of 2-Butyne, and of C_2H_4 . The coprecipitation of $V(OH)_2$ with $Mg(OH)_2$ with 8 N KOH produces mixed hydroxide gels which react with C_2H_2 to yield C_2H_4 . At sufficiently low concentrations of C_2H_2 , some of the product C_2H_4 is also reduced, giving rise to C_2H_6 . At high concentrations of C_2H_2 , C_2H_4 is formed almost exclusively and the reaction goes to completion within 2–3 min (Figure 1). In typical experiments, $Mg(OH)_2$ (2000 μmol), containing 35 μmol of $V(OH)_2$, was reacted with C_2H_2 at 1 atm of pressure. After 10 min of reaction at 23 °C, the total yield of C_2H_4 was 32 μmol , indicating that $V(OH)_2$ acts as a two-electron reductant under these conditions. This was confirmed by the determination of the oxidation state of vanadium in the terminal reaction mixtures. Addition of 1,10-*o*-phenanthroline and subsequent acidification produced the complex of V^{4+} , which was identified spectrophotometrically (see Experimental Section).

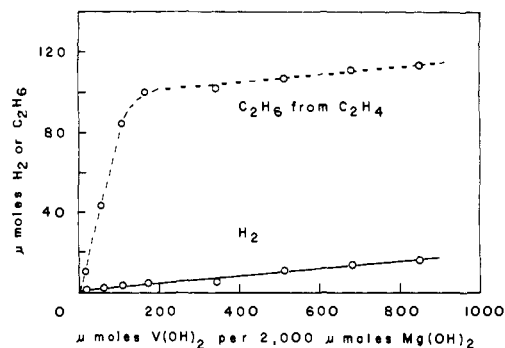


Figure 3. Reduction of C_2H_4 and H_2 evolution as a function of the V^{2+} content of $Mg(OH)_2$. Conditions as described in legend to Figure 2.

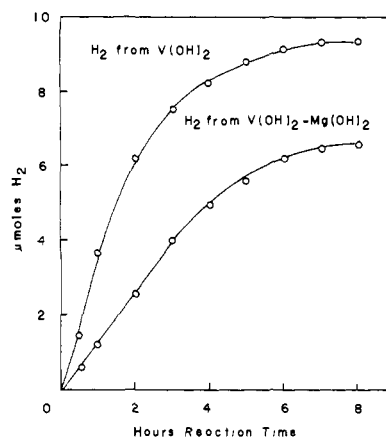
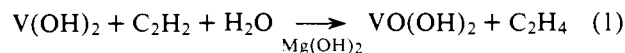


Figure 4. Time dependence of H_2 evolution from 35 μmol of $V(OH)_2$ and from 35 μmol of $V(OH)_2$ coprecipitated with 2000 μmol of $Mg(OH)_2$ in 8 N NaOH at 25 °C.

In view of these results, the reduction of C_2H_2 by $V(OH)_2$ - $Mg(OH)_2$ is formulated as shown in eq 1:



The yields of C_2H_4 increase linearly with the $V(OH)_2$ concentration in the $Mg(OH)_2$ at least up to the V^{2+}/Mg^{2+} ratio of about 1/5. Above this ratio, C_2H_4 production declines somewhat while H_2 is formed in higher yields (Figure 2). With pure $V(OH)_2$ considerably more H_2 is generated (e.g., 8.0 μmol from 35 μmol of $V(OH)_2$) and the yields of C_2H_4 drop (to 23 μmol), corresponding to 65% of the theoretical amount. The combined yields of C_2H_4 and H_2 correspond to 88% of the theoretical electron transfer efficiency.

The reduction of C_2H_4 to C_2H_6 occurs at a slower rate than that of C_2H_2 to C_2H_4 (Figure 1). After 6 h of reaction, a virtually quantitative conversion has been observed (i.e., one molecule of C_2H_6 is formed per mole of $V(OH)_2$). Moreover, V^{2+} is oxidized to V^{4+} , as evidenced by the 1,10-*o*-phenanthroline assay. The reduction of C_2H_4 thus follows the stoichiometry given in eq 2:



Figure 3 shows that the yields of C_2H_6 increase linearly with the concentration of $V(OH)_2$ in the $Mg(OH)_2$ host lattice up to the V^{2+}/Mg^{2+} ratio of 1/20, while the yields of H_2 are proportional to the V^{2+} concentration in the gels at least up to the V^{2+}/Mg^{2+} ratio of 1/2. Under the optimal conditions for C_2H_2 reduction, 2-butyne is also reduced. The product was identified as *cis*-2-butene, the *trans* isomer is not formed.

Hydrogen Evolution. Freshly precipitated $V(OH)_2$ reacts with water to yield H_2 . Its incorporation into the $Mg(OH)_2$

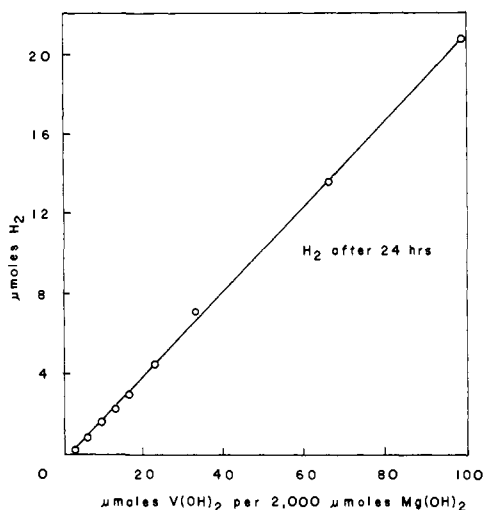


Figure 5. Yields of H_2 from $V(OH)_2$ - $Mg(OH)_2$ gels after 24 h of reaction at 25 °C as a function of increasing V^{2+} content of $Mg(OH)_2$ under 1 atm of argon.

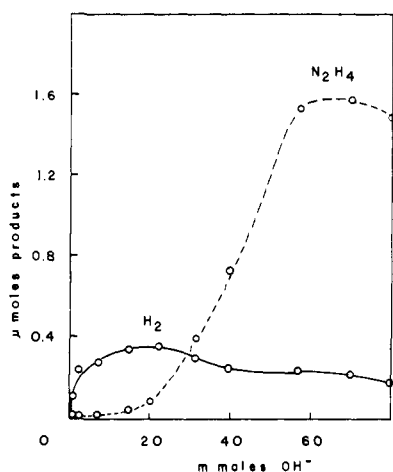
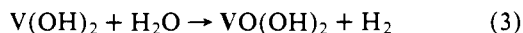


Figure 6. Dependence of the yields of N_2H_4 and H_2 on the concentration of the added base. The $V(OH)_2$ - $Mg(OH)_2$ gels contained 35 μmol of V^{2+} at $t = 0$ in 2000 μmol of $Mg(OH)_2$. Yields were measured after 20 min of reaction at 25 °C and 1 atm of N_2 .

host lattice causes a retardation of H_2 evolution as shown in Figure 4. The yields of H_2 increase linearly with the $V(OH)_2$ content of $Mg(OH)_2$ at least up to the V^{2+}/Mg^{2+} ratio of 1/20 (Figure 5). After prolonged reaction times, V^{4+} was detected in the acidified reaction solutions, indicating that $V(OH)_2$ is oxidized by a two-electron process just as in the reactions with the acetylenic or olefinic substrates. The main process of H_2 evolution is accordingly expressed in terms of eq 3:



Reduction of Molecular Nitrogen. (a) Reaction Conditions and Products. Shilov et al. previously demonstrated that $V(OH)_2$ reduces N_2 only in strongly alkaline media and in the presence of $Mg(OH)_2$.⁴ The alkaline reaction conditions are required primarily to suppress the evolution of H_2 . Figure 6 indicates that H_2 production declines as $[OH^-]$ increases and N_2H_4 is formed. With pure $V(OH)_2$, H_2 is evolved, albeit at a slower rate. However, in the presence of N_2 in the gas phase, the H_2 formation is somewhat *stimulated* relative to reactions under argon, an effect which will be discussed below. It is essential that the $V(OH)_2$ is incorporated into the $Mg(OH)_2$ lattice, i.e., precipitated simultaneously by the addition of alkali to solutions of V^{2+} (aq) and Mg^{2+} salt. If $Mg(OH)_2$ is made first and V^{2+} (aq) is added later, H_2 is evolved, and only traces

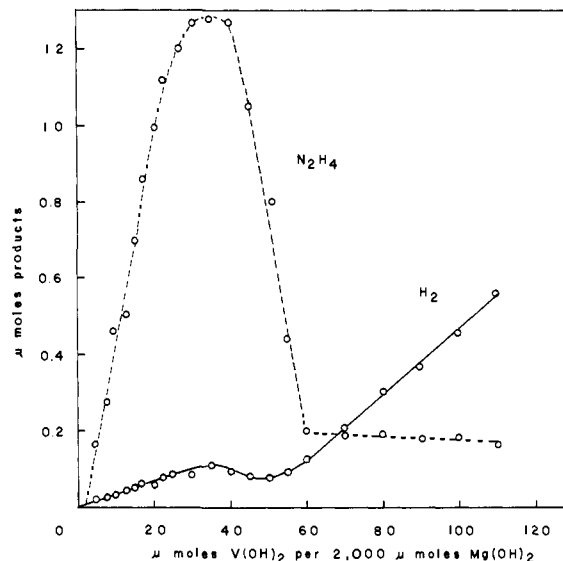


Figure 7. Yields of N_2H_4 and of H_2 from $V(OH)_2$ - $Mg(OH)_2$ as a function of increasing initial V^{2+} concentration, measured after 20 min of reaction at 25 °C and 1 atm of N_2 .

of N_2 are reduced to N_2H_4 . The yields of N_2H_4 are also affected by the presence of anions. Sulfate, CO_3^{2-} , and PO_4^{3-} lower the yields, as well as a variety of complexing agents.¹⁰ Earlier attempts to replace $Mg(OH)_2$ as the $V(OH)_2$ host matrix failed to produce reactive systems. Since the metal hydroxides must be nonamphoteric and inert under the reaction conditions, the number of potential candidates is relatively small. Moreover, the isomorphous substitution of metal ions by V^{2+} will also depend to some extent on the crystal structure of the host lattice. Thus, attempts to coprecipitate $V(OH)_2$ with $La(OH)_3$ or $Y(OH)_3$ failed to produce N_2 -reducing gels. Somewhat active systems were obtained with ZrO_2 -aq coprecipitated with $V(OH)_2$, however, as will be outlined below. With $V(OH)_2$ in the absence of $Mg(OH)_2$ only traces of N_2H_4 and NH_3 are formed. With $V(OH)_2/Mg(OH)_2$ at 0–25 °C, N_2 is reduced virtually exclusively to N_2H_4 . At temperatures between 70 and 90 °C, a secondary reduction of N_2H_4 to NH_3 occurs.⁴ We have confirmed this observation and therefore conducted our experiments at room temperature where only traces of NH_3 are formed. The optimal yields of N_2H_4 from N_2 at 1 atm of pressure were only in the order of 15% based on the total amount of V^{2+} . The low efficiency of N_2 reduction relative to that of C_2H_2 is largely due to the much lower solubility of nitrogen in the reaction medium. At elevated N_2 pressures more N_2H_4 is formed,⁴ but we decided to run all our experiments at atmospheric pressure.

(b) Dependence of N_2H_4 Yields on V^{2+} . The yields of N_2H_4 depend critically on the concentration of V^{2+} in the host lattice. They increase linearly with V^{2+} up to a critical V^{2+}/Mg^{2+} ratio, beyond which an abrupt decline is observed while H_2 -evolution increases (Figure 7). Coprecipitation of $V(OH)_2$ with ZrO_2 -aq produces gels of approximately 10% of the N_2 -reducing activity of $V(OH)_2$ - $Mg(OH)_2$, the dependence of the yields of N_2H_4 and H_2 on the V^{2+} concentration in this host lattice shows similarities, however, as may be seen in Figure 8. At 25 °C, N_2 is again reduced predominantly to N_2H_4 , and hardly at all to NH_3 . In spite of the anomalous course of the reaction at high V^{2+} concentrations in the gels, the apparent linear dependence of the yields of N_2H_4 on $[V^{2+}]$ up to nearly the optimal V^{2+} /host ratios suggests that the reduction of N_2 involves a two-electron transfer step. Since C_2H_2 is reduced to C_2H_4 it is reasonable to assume that N_2 is initially reduced to N_2H_2 rather than directly to N_2H_4 . As in the reduction of

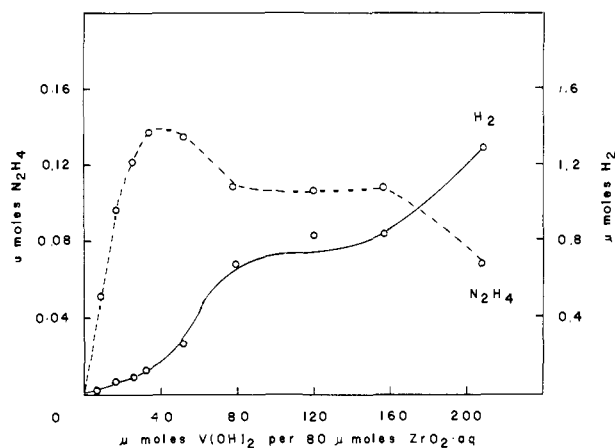


Figure 8. Yields of N_2H_4 and of H_2 from $V(OH)_2$ - ZrO_2 :aq as a function of increasing initial V^{2+} concentration, measured after 20 min of reaction at 25 °C and 1 atm of N_2 .

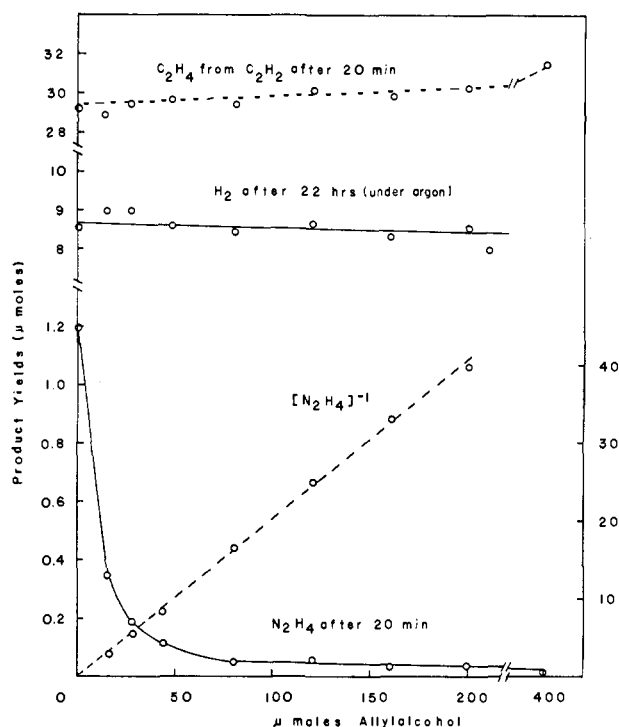


Figure 9. Effect of allyl alcohol on C_2H_2 reduction, H_2 production, and the yields of N_2H_4 in the presence of N_2 as the substrate at 1 atm, and 25 °C. Gels of 2000 μmol of $Mg(OH)_2$ contained 35 μmol of $V(OH)_2$ at $t = 0$. Also shown is a plot of $[N_2H_4]^{-1}$ vs. the concentration of allyl alcohol, demonstrating the second-order mechanism of N_2H_2 quenching by allyl alcohol.

the unsaturated organic substrates, the presence of V^{4+} in the terminal reaction suspensions was demonstrated by means of the 1,10-phenanthroline assay.

(c) **Effect of Added V^{3+} and V^{2+} .** The addition of V^{3+} to $V(OH)_2$ - $Mg(OH)_2$ systems has been shown⁶ to prevent N_2H_4 formation. This observation was confirmed, but we also noted that the addition of the same amount of V^{2+} has the same effect. Aside from diminishing the N_2 -reducing capacity of the gels, the addition of V^{3+} increases H_2 evolution (see Table II).

(d) **Diimide Trapping Experiments.** To detect N_2H_2 in different N_2 -reducing systems we previously employed fumarate or *cis*-4,5-cyclohexenedicarboxylate as trapping agents.⁸ Both compounds are known to be reduced by N_2H_2 to the corresponding saturated derivatives. However, these trapping agents appear to prevent incorporation of $V(OH)_2$ into the $Mg(OH)_2$

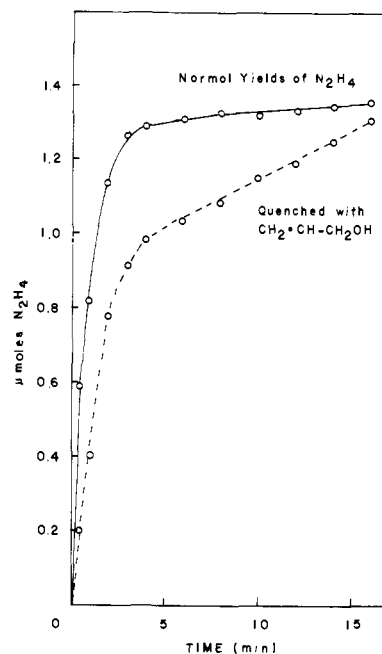


Figure 10. Effect of addition of allyl alcohol (150 μmol) on the yields of N_2H_4 as a function of quenching time compared with the yields observed under standard conditions.

host lattice and thus could not be used in the present study. We therefore selected allyl alcohol for this purpose, as it is also efficiently reduced by N_2H_2 ,¹¹ but does not interfere with the gel-forming processes. Allyl alcohol is only slowly reduced by $V(OH)_2$ and does not inhibit H_2 evolution or C_2H_2 reduction. This is shown in Figure 9, together with its effect on N_2H_4 formation. At concentrations of allyl alcohol as low as 10 μmol per 35 μmol of $V(OH)_2$ a 50% inhibition of N_2H_4 production is seen. Furthermore, a plot of $[N_2H_4]^{-1}$ vs. [allyl alcohol] is linear. Analysis of the reaction solutions revealed that 1-propanol is formed from allyl alcohol, preferentially when N_2 is present as the substrate. For example, a suspension of $V(OH)_2$ - $Mg(OH)_2$ containing 35 μmol of V^{2+} and 45 μmol of allyl alcohol (initial concentrations) produced 6.8 μmol of 1-propanol after 1 h of reaction at 25 °C and 1 atm of N_2 . Identical experiments under 1 atm of argon or C_2H_2 , in contrast, yielded only 0.5–0.8 μmol of 1-propanol (see Experimental Section). Since allyl alcohol is not reduced by N_2H_4 , this result demonstrates that N_2H_2 is an intermediate in the reduction of N_2 to N_2H_4 in the present system.

Addition of excess allyl alcohol to reacting $V(OH)_2$ - $Mg(OH)_2$ suspensions under N_2 at various time-points caused a lowering of the yields of N_2H_4 relative to normally run controls (Figure 10). This shows that diimide rapidly accumulates in the reaction mixture and that its subsequent disproportionation to N_2H_4 and N_2 occurs at a finite rate. The difference plot in Figure 11 shows that the concentrations of N_2H_2 reach a maximum during the first 2 min of reaction. The disappearance of N_2H_2 follows a second-order rate law as evidenced by the linear dependence of $[N_2H_2]^{-1}$ as a function of time.

(e) **Effect of N_2 on H_2 Evolution from $V(OH)_2$.** The abrupt decline of the N_2H_4 yields in the reaction of N_2 with gels at higher than the optimal V^{2+}/Mg^{2+} ratio (Figure 7), and the virtual ineffectiveness of $V(OH)_2$ as a reductant of N_2 in the absence of $Mg(OH)_2$ suggested that N_2 is either not reduced under these conditions or that $V(OH)_2$ catalyzes the decomposition of N_2H_2 into the elements. Whereas C_2H_2 inhibits H_2 production from $V(OH)_2$ relative to runs under argon, N_2 has a significant stimulatory effect, as is shown in Figure 12. The addition of allyl alcohol abolishes the enhancement of H_2

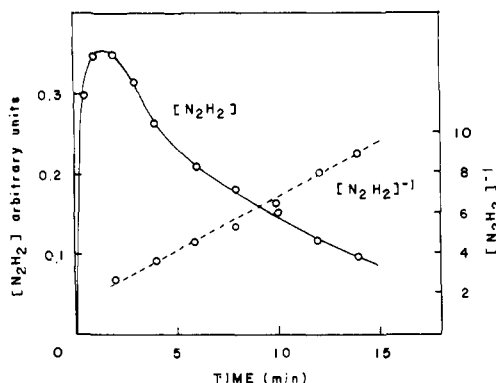


Figure 11. Difference plot of the N_2H_4 yields of reactions quenched with and without allyl alcohol. Data are from Figure 10. The linear dependence of $[\text{N}_2\text{H}_2]^{-1}$ on time demonstrates that the disproportionation of N_2H_2 into N_2 and N_2H_4 is a second-order process.

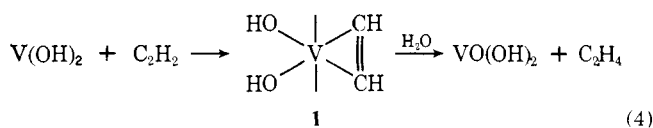
production by N_2 but has only a slight effect on the rate of H_2 formation under argon. It thus appears that N_2 reacts with $\text{V}(\text{OH})_2$ also in the absence of $\text{Mg}(\text{OH})_2$, but the N_2H_2 produced decomposes into N_2 and H_2 more rapidly than it disproportionates into N_2 and N_2H_4 .

Stimulation of H_2 Evolution and of Substrate Reduction in Acidic Solutions of V^{2+} (aq) by UV Light. Whereas the reactions of $\text{V}(\text{OH})_2$ and of $\text{V}(\text{OH})_2\text{-Mg}(\text{OH})_2$ with substrates are not markedly influenced by irradiation of the gels with uv light, a stimulation of H_2 evolution and of the reduction of C_2H_2 as well as of C_2H_4 in acidic solutions of V^{2+} (aq) has been observed. Under similar conditions, traces of N_2 are reduced to NH_3 . The corresponding reactions occur only very slowly, or not at all, in the dark or on irradiation with visible light.

Discussion

Reduction of Acetylenic and Olefinic Substrates in the $\text{V}(\text{OH})_2\text{-Mg}(\text{OH})_2$ System. The present work demonstrates that $\text{V}(\text{OH})_2$ coprecipitated with $\text{Mg}(\text{OH})_2$ acts as a two-electron reductant in reactions with acetylenic and olefinic substrates. The observed linear dependence of the product yields on the concentration of V^{2+} in the $\text{Mg}(\text{OH})_2$ gels, the near quantitative conversions, and the detected presence of V^{4+} after completion of the reactions are consistent with a mechanism in which one molecule of the substrate interacts with one V^{2+} center. We have obtained no evidence for the occurrence of disproportionation reactions of $\text{V}(\text{OH})_2$ prior to interaction with the substrates and hence conclude that V^{2+} ions are the actual reactive species.

Our work also does not suggest that the reactions require a specific arrangement of two or more V^{2+} ions in the $\text{Mg}(\text{OH})_2$ lattice; in fact, the observed reaction stoichiometry alone indicates that the V^{2+} species are mononuclear and act independently of each other. Acetylene must interact with V^{2+} in the side-on fashion, since 2-butyne is selectively reduced to *cis*-2-butene. The overall process of C_2H_2 reduction is accordingly formulated by eq 4. An analogous mechanism is



proposed for the reduction of C_2H_4 to C_2H_6 . The oxidative addition of the acetylenic or olefinic substrates to the $\text{V}(\text{OH})_2$ centers must be the rate-determining steps in these reactions. The subsequent hydrolysis of organovanadium intermediates such as **1** occurs rapidly even under the strongly alkaline reaction conditions.

Since the reduction of the unsaturated substrates by

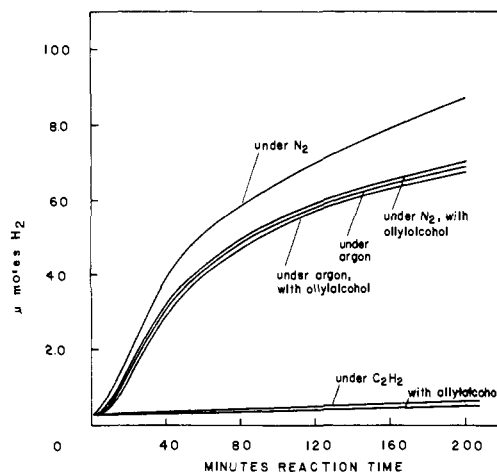


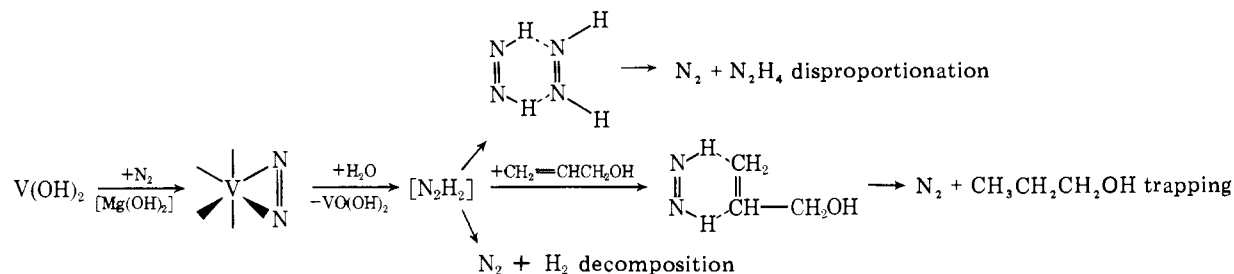
Figure 12. Time dependence of H_2 evolution from $\text{V}(\text{OH})_2$ ($35 \mu\text{mol}$ at $t = 0$) in 8 N KOH under 1 atm of N_2 , C_2H_2 , or argon, in the presence or absence of allyl alcohol ($29 \mu\text{mol}$), at 25°C .

$\text{V}(\text{OH})_2\text{-Mg}(\text{OH})_2$ is virtually quantitative, this indicates that a reduction of V^{4+} by remaining V^{2+} to V^{3+} does not take place. This may no longer be the case in the analogous reactions with $\text{V}(\text{OH})_2$ in the absence of $\text{Mg}(\text{OH})_2$. With C_2H_2 the conversion to C_2H_4 under these conditions was only in the order of 65%. Incorporation of $\text{V}(\text{OH})_2$ into the $\text{Mg}(\text{OH})_2$ lattice thus may prevent V^{2+} consuming side reactions such as the oxidation by V^{4+} mentioned above.

Hydrogen Evolution. Vanadous hydroxide may be regarded as a reducing metallonucleophile, whose reduction potential is sufficient to cause H_2 evolution even in strongly alkaline protic media. Since the formation of H_2 is an undesirable side-reaction, it thus can be understood why the reduction of substrates such as N_2 occurs optimally under conditions at which H_2 evolution is minimized. The mechanism of H_2 evolution was not investigated in any detail but is assumed to involve hydridovanadium species as reactive intermediates.

Nitrogen Reduction. Shilov's suggestion⁶ that N_2 is reduced by arrangements of four V^{2+} ions in the $\text{Mg}(\text{OH})_2$ host lattice directly to hydrazine is not supported by the present investigation. Instead, our work clearly indicates that N_2H_2 is formed initially, and since allyl alcohol is reduced to 1-propanol under the conditions of N_2 fixation, we conclude that N_2H_2 is generated in the free state by the hydrolysis of a vanadium-nitride-type intermediate. We propose that V^{2+} reacts with N_2 in the side-on fashion just as with the isoelectronic alkynes. Since 2-butyne is reduced specifically to *cis*-2-butene, we furthermore postulate that the *cis* isomer of N_2H_2 is generated in the hydrolysis of the vanadium nitride intermediate. All subsequent reactions of N_2H_2 which we have observed in the present systems are fully consistent with the known behavior of this reactive species¹² and are summarized in Scheme I. In the $\text{V}(\text{OH})_2\text{-Mg}(\text{OH})_2$ systems, the disproportionation of N_2H_2 into N_2 and N_2H_4 is the main reaction at 25°C up to the optimal $\text{V}^{2+}/\text{Mg}^{2+}$ ratio. The results of the quenching experiments suggest that this reaction occurs as a second-order process (see Figures 10 and 11), in accord with similar observations with gaseous N_2H_2 .¹² The demonstrated reduction of allyl alcohol to 1-propanol by the N_2H_2 generated under our reaction conditions proves that the vanadium-nitride intermediate must have undergone hydrolysis to yield what we define as "free" diimide, even though it could be solvated or stabilized within the $\text{Mg}(\text{OH})_2$ host lattice.

The observed linear dependence of $[\text{N}_2\text{H}_4]^{-1}$ on the concentration of allyl alcohol in the experiment of Figure 9 indicates that the hydrogenation of allyl alcohol by N_2H_2 follows a second-order rate law. This is again in complete accord with

Scheme I. Proposed and Observed Reactions of N_2 and of N_2H_2 in the $V(OH)_2$ - $Mg(OH)_2$ System

published^{13,14} experimental evidence on the reduction of olefinic substrates by chemically generated N_2H_2 such as the reaction with dihydrodicyclopentadiene in glycol monomethyl ether/ethanol with N_2H_2 prepared from benzenesulfonyl hydrazide at 77.8 °C.

It is of interest that diphenylacetylene is not reduced by N_2H_2 in 2.5 N KOH/glycol monomethyl ether, while styrene is hydrogenated to 77% under the same conditions.¹³ It thus is not surprising that Lorenz et al.⁷ were unable to detect N_2H_2 as the intermediate of N_2 reduction in the $V(OH)_2$ - $Mg(OH)_2$, for they employed diphenylacetylene as the trapping agent.

The incorporation of V^{2+} into the $Mg(OH)_2$ host matrix is probably necessary to provide a large active surface for reaction with N_2 and to suppress H_2 evolution, which is an undesirable V^{2+} -consuming side-reaction. It is possible that $Mg(OH)_2$ and, to some extent, also $ZrO_2 \cdot aq$ stabilize N_2H_2 against decomposition into the elements. From the yields of H_2 under optimal conditions of N_2 reduction in the $V(OH)_2$ - $Mg(OH)_2$ system at 25 °C (see Figure 7), it follows that the decomposition of N_2H_2 into N_2 and H_2 occurs to only a minor extent. Since the decomposition of N_2H_2 into the elements is base-catalyzed¹³ and this reaction is evidently not favored if the N_2H_2 is generated within suitable host-lattices, we conclude that the effective concentration of OH^- in the metallohydroxide aggregates is probably lower than in the surrounding homogeneous phase.

The decomposition of N_2H_2 has been studied in the gas phase and is a first-order reaction¹² whose rates are strongly surface-dependent. The reaction of N_2 with $V(OH)_2$ in the absence of $Mg(OH)_2$ produces virtually no N_2H_4 but enhances the evolution of H_2 . Since this effect of N_2 on H_2 production disappears in the presence of allyl alcohol (see Figure 12) we conclude that N_2H_2 is still formed but that its decomposition into the elements is catalyzed by base as well as by vanadium hydroxides outside the $Mg(OH)_2$ host lattice. This conclusion is also supported by the experiments in which either V^{3+} or V^{2+} is added in excess to the optimal $V(OH)_2$ - $Mg(OH)_2$ N_2 -fixing system; both ions depress the yields of N_2H_4 . However, V^{3+} also stimulates the N_2 -independent H_2 production (see Table II).

Light-Stimulated Reactions of V^{2+} (aq). Whereas none of the substrate reactions of $V(OH)_2$ gels could thus far be stimulated by irradiation with visible or uv light, our observation that V^{2+} (aq) is activated on photoexcitation is of interest. In view of the inertness of V^{2+} (aq) in ligand substitution processes, we ascribe the effect to a photodeauration which is followed by the reaction with the substrates. Whereas H_2 -evolution and C_2H_2 - and C_2H_4 -reduction are efficiently stimulated by uv-light, the light-induced reduction of N_2 produces only traces of ammonia under the same conditions.

Comparison with Other Nitrogen Reducing Systems. Previous work has indicated that diimide is the intermediate in the reduction of molecular nitrogen to hydrazine and ammonia in the molybdothiol and molybdocyano model systems of nitrogenase.^{8,9} The work described in the present paper has led to the same conclusion and also revealed a number of mechanistic

analogies between substrate reactions of V^{2+} and Mo^{4+} compounds. It is possible that diimide is the intermediate in other metal-promoted reductions of N_2 in protic media as well. Hence, a crucial problem in the design of efficient N_2 -reducing catalytic systems operating in water as the solvent resides in the prevention of diimide decomposition.

Experimental Section

Reagents and Chemicals. All reagents and chemicals were commercially available and of analytical or reagent grade purity, and were used without further purification.

Vanadium(II) Stock Solution. For most experiments, a vanadium(II) stock solution was prepared as follows: Vanadyl sulfate, $VO(SO_4) \cdot xH_2O$, 8.0 g, and 10 g of mossy zinc were placed into a glass bottle of 160-ml capacity. The bottle was flushed with pure argon for 20 min and sealed with a rubber serum cap. Thereafter, 100 ml of 1 N HCl was injected. To alleviate the pressure buildup due to the formation of hydrogen, excess gas was withdrawn from the bottle by means of a large syringe at 5-min intervals. The reduction of V^{4+} to V^{2+} occurs within ca. 3 h of reaction at room temperature. Before each experiment, the concentration of V^{2+} (aq) in the solutions was determined spectrophotometrically as outlined in ref 15, or by titration with Ce^{4+} solution.¹⁶ The values obtained by the two methods agreed within $\pm 3\%$.

Typical Experimental Procedure for C_2H_2 or C_2H_4 Reduction. Aliquots of the V^{2+} (aq) stock solution (usually 0.2–0.4 ml), 2 ml of CH_3OH and 1 ml of a 2 M $MgCl_2$ solution in 1 N HCl were injected into glass bottles of 38-ml capacity, which were sealed with silicone rubber serum caps. The glass bottles were previously filled with either C_2H_2 or C_2H_4 at 1 atm. Subsequently, 7.0 ml of 8 N KOH was injected as rapidly as possible while the reaction flasks were shaken. At convenient time-points, gas samples were withdrawn and analyzed for C_2H_2 , C_2H_4 , and C_2H_6 by gas-liquid-phase chromatography (GLC), using a Varian, Series 1200 Aerograph instrument, equipped with a 6 ft Durapak phenylisocyanate-porasil, 80–100 mesh, column. The hydrocarbons were identified as usual by measurement of the retention times and coinjection of authentic samples, the reproducibility of the yield-measurements is within $\pm 1.5\%$. The experiments were modified by changing the concentrations of the reactants, i.e., by varying the V^{2+}/Mg^{2+} ratio. For runs at substrate-pressures of below 1 atm, the reaction bottles were first filled with pure argon and the gaseous substrates were injected by means of a syringe.

Reduction of 2-Butyne. The formation of *cis*-2-butene from 2-butyne was demonstrated by adding 0.2 ml of 2-butyne to argon-filled glass bottles. The reduction experiments were performed as described above. For GLC analysis, gas samples were withdrawn after 24 h of reaction at 25 °C. The product, *cis*-2-butene, was identified by co-chromatography with authentic *cis*- and *trans*-2-butene.

Hydrogen Production. The evolution of H_2 during the reactions was followed under the conditions outlined above, both in the absence and presence of reducible substrates. The yields of H_2 were determined by GLC, using a column of 6 ft length, filled with molecular sieve (5 A), at the operating temperature of 27 °C.

Nitrogen Reduction. The N_2 -fixation experiments were performed as outlined for C_2H_2 or C_2H_4 , except that the reaction flasks were filled with pure N_2 at 1 atm of pressure. In typical runs, the reaction flasks were opened after 20 min of reaction at room temperature. The solutions were centrifuged to remove the magnesium and vanadium hydroxide residue. The supernatant solution was carefully acidified to pH 1 by addition of 6 N HCl, and diluted to a volume of 25 ml. Hydrazine was determined colorimetrically according to the method of Watt and Chrisp,¹⁷ except that the hydrazone of *p*-dimethylami-

Table I. Yields of 1-Propanol from Reactions of V(OH)₂-Mg(OH)₂ Gels in the Presence of 45 μmol of Allyl Alcohol. Gels Contained 35 μmol of V(OH)₂ and 2000 μmol of Mg(OH)₂. Reaction Time: 45 min

Substrate ^a	1-Propanol μmol
N ₂	4.8
C ₂ H ₂	0.5
C ₂ H ₄	0.5
None (argon)	ca. 0.8

^a All at 1 atm of pressure in the gas phase at 27 °C.

nobenzaldehyde was extracted into a measured volume of CH₂Cl₂.⁸ In some experiments, the reaction suspensions were distilled and the distillates analyzed for N₂H₄ and NH₃. Under these conditions of workup, a complete reduction of N₂H₄ to NH₃ was observed.

Nitrogen Reduction with V(OH)₂-ZrO₂-aq Systems. A 0.2 F solution of Zr⁴⁺ was prepared by dissolving 5.0 g of Zr(O-*i*-C₃H₇)₄ in 95 ml of CH₃OH containing 5 ml of 12 N HCl. In typical experiments, 0.8 ml of this solution was injected into N₂-filled reaction flasks, followed by 0.1–0.4 ml of V²⁺ (aq) stock solution. The ZrO₂-aq-V(OH)₂ gels were precipitated by adding 7.0 ml of 8 N KOH, and the ensuing reaction with N₂ was allowed to proceed for about 20 min. After removal of the metal hydroxide gels by centrifugation, N₂H₄ was determined colorimetrically as outlined in the preceding section. The freshly precipitated V(OH)₂-Mg(OH)₂ gels as well as those of V(OH)₂-ZrO₂-aq are initially yellow-brown. On reaction they gradually attain a greenish color. We have found empirically that N₂ reduction to N₂H₄ with V(OH)₂-metal hydroxide or -oxide systems occurs only if the gels are initially yellow-brown. Some gels turn violet instead, and these invariably failed to reduce N₂ to N₂H₄. The results of typical experiments are represented graphically in Figure 8.

Diimide Trapping Experiments. The diimide trapping experiments were performed under the standard conditions for N₂ reduction except that known amounts of allyl alcohol (freshly distilled) were added in CH₃OH solution. The formation of 1-propanol from allyl alcohol in the presence of N₂ as the substrate was demonstrated by adding 45 μmol of allyl alcohol prior to the injection of 8 N KOH. 1-Propanol and remaining allyl alcohol was determined by GLC in gas samples withdrawn at various time-points. Gas-chromatographic analysis was performed on a Varian, Series 1200 Aerograph instrument, equipped with a 6 ft Poropak Q filled column, operating at 150 °C. Allyl alcohol and 1-propanol were identified by coinjection of authentic samples. The results of typical experiments are given in Table I.

Effects of V³⁺ and of V²⁺ on N₂ Reduction by V(OH)₂-Mg(OH)₂ Gels. To test the effect of V³⁺ and of V²⁺ on the N₂ reducing activity of V(OH)₂-Mg(OH)₂ gels, solutions containing V²⁺ (aq) and V³⁺ (aq) were coprecipitated with Mg²⁺ from 1 N HCl solutions under 1 atm of N₂, by injecting 7 ml of 8 N KOH. The yields of H₂ were determined by withdrawing gas samples after 20 min of reaction; colorimetric assays for N₂H₄ in the reaction suspensions were performed immediately after the H₂ measurements. The results are summarized in Table II.

Phenanthroline Assay for V(IV). A 0.10 M solution of 1,10-*o*-phenanthroline in 95% ethanol was prepared and stored in an argon-filled, rubber-serum-capped glass bottle. In typical experiments, 2.0 ml of this solution was added to the reaction solutions after they had been previously acidified with 12 N HCl to the pH of about 1. It is essential to perform the acidification under the complete exclusion of air to prevent secondary oxidation of lower-valent vanadium species. Samples of the resulting colored solutions were withdrawn by means of a syringe and injected into capped, argon-filled cuvettes. The V⁴⁺ complex of 1,10-*o*-phenanthroline¹⁸ exhibits a characteristic absorption spectrum with λ_{max} of 500 nm (ε 3 × 10³) and shoulders at 468 and 420 nm, respectively. Addition of 1,10-*o*-phenanthroline to solutions of V³⁺ in 1 N HCl produces a spectrum with a characteristic

Table II. Effects of Added V(II) and V(III) on N₂H₄ Yields and H₂-Production in the V(OH)₂-Mg(OH)₂ System at Optimal V²⁺/Mg²⁺-Ratio^a

μmol of added	Yields, μmol, of		
	V ²⁺	V ³⁺	N ₂ H ₄
35	0	1.4	0.25
35	20	0.9	0.75
35	55	0.6	2.2
35	70	0.3	3.5
35 + 20	—	0.45	0.12
35 + 35	—	0.19	0.20
35 + 65	—	0.18	0.45

^a The concentration of Mg(OH)₂ was 2000 μmol in all cases. The experiments were performed under 1 atm of N₂ at 25 °C as outlined under "Nitrogen Reduction".

absorption at 624 nm. Solutions of V²⁺ in the presence of 1,10-*o*-phenanthroline show an absorption maximum at 580 nm and a shoulder at 525 nm. Suspensions which still contain V(OH)₂ in addition to VO(OH)₂ yield V³⁺ on acidification. It is important, therefore, to run these experiments after the substrate reduction by V(OH)₂ is as nearly complete as possible.

Uv-Light Induced Substrate Reduction by V²⁺ (aq). A freshly prepared, 0.085 M solution of V²⁺ (aq) in 1 N HCl, usually 10 ml, was injected into Pyrex bottles of 170 ml total capacity which either contained pure argon or mixtures of argon with C₂H₂ or C₂H₄. The photochemical reactions were performed by exposing the reaction flasks to uv light emitted from a high intensity (360 W) mercury-arc lamp at a distance of 6 in.; the flasks were cooled with ice during the irradiation. For hydrocarbon analysis or the determination of H₂, gas samples were withdrawn at convenient time-points, usually after 40–120 min of irradiation. Control experiments in the dark were also performed. These showed that the reactions were genuinely light-induced. In the presence of N₂ at 1 atm of pressure, traces of NH₃ (0.5–0.8 μmol) were detected both colorimetrically and by mass-spectrographic analysis using ¹⁵N₂ as the substrate.

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