# Hydrogen Evolving Systems. 3. Further Observations on the Reduction of Molecular Nitrogen and of Other Substrates in the V(OH)$_2$–Mg(OH)$_2$ System

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**Abstract:** In the V(OH)$_2$–Mg(OH)$_2$ nitrogen fixing system, originally described by Shilov and co-workers, N$_2$ is reduced to diimide, N$_2$H$_2$. The Mg(OH)$_2$ host lattice provides an environment in which N$_2$H$_2$ can accumulate without suffering rapid base-catalyzed decomposition into the elements. Owing to the lower effective alkalinity inside the Mg(OH)$_2$ lattice, N$_2$H$_2$ can *disproportionate* instead to N$_2$ and N$_2$H$_4$. If "V(OH)$_2$–Mg(OH)$_2$" gels are precipitated from solutions containing 5–20% CH$_3$OH, higher yields of N$_2$H$_4$ are observed presumably because the aging of the hydroxide gels is retarded and/or the V$^{2+}$ sites become more accessible to diffusing N$_2$. Such gels possess the properties of *molecular sieves* inasmuch as N$_2$ reduction is inhibited significantly only by C$_2$H$_6$ or C$_3$H$_8$, but not by CH$_4$ or C$_4$- or longer chain hydrocarbons. Several new experiments are described which reaffirm the diimide mechanism of N$_2$ reduction, including inhibition studies by CO and CN$^-$. V(OH)$_2$ behaves as a two-electron reductant even with diazirine, diazomethane, butadiene, and substituted or unsubstituted alkynes. The stereochemistry of C$_2$H$_2$ reduction is shown to be cis. Alkyl halides are reductively dehalogenated to yield unrearranged alkanes.

In part 2 of this series[1] we reported that aqueous suspensions of V(OH)$_2$ in inert host lattices such as Mg(OH)$_2$ or ZrO$_2$·aq reduce molecular nitrogen to hydrazine via diimide (diazene), N$_2$H$_2$, as the intermediate (Scheme I).

The V(OH)$_2$–Mg(OH)$_2$ nitrogen fixing system, originally discovered by Shilov et al.,[2] has remained mechanistically obscure as N$_2$ was assumed[3] to be reduced *directly* to N$_2$H$_4$, and arguments were presented which seemed to render diimide an unlikely intermediate on theoretical grounds.[4,5]

However, our work[1] showed that V(OH)$_2$ reduces N$_2$ to N$_2$H$_2$, which itself is not reduced and either disproportionates or decomposes as outlined in Scheme I. Since this mechanism of N$_2$ reduction is very similar to that in the molybdenum-based model systems of nitrogenase,[6] an independent system for the study of the reduction of N$_2$ via N$_2$H$_2$ became available as a means of testing our nitrogenase mechanism. However, the V(OH)$_2$–Mg(OH)$_2$ N$_2$-fixing system is also of interest in its own right and still poses numerous intriguing questions. Does V(OH)$_2$ behave as a two-electron reductant also with respect to substrates that could accept more than two electrons? Are there other means to demonstrate the intermediacy of diimide? What is the role of the Mg(OH)$_2$ host lattice? Are there alternative interpretations? We shall address ourselves to these and other questions in the following.

## Results

**Reactions of V(OH)$_2$–Mg(OH)$_2$ with Substrates Other Than N$_2$.** Our previous work has indicated that V(OH)$_2$ acts as a two-electron reductant even with substrates that could in principle accept more electrons. At high concentrations, C$_2$H$_2$ is reduced to C$_2$H$_4$, and V$^{2+}$ is oxidized to V$^{4+}$ virtually *quantitatively*, in accord with the proposed two-electron re-

duction mechanism. Side-on interaction of C$_2$H$_2$ with V$^{2+}$ was considered probable in view of the observed reduction of 2-butyne to *cis*-2-butene.[1] By conducting the reduction of C$_2$H$_2$ in D$_2$O, we have since proved the cis stereochemistry of C$_2$H$_2$ reduction as well (see Experimental Section). At low concentrations of C$_2$H$_2$, a mixture of C$_2$H$_4$ and C$_2$H$_6$ is formed due to the secondary reduction of product C$_2$H$_4$, which is also a substrate in the V(OH)$_2$–Mg(OH)$_2$ system.[1] Our work thus does not support the view according to which substrates are reduced by one-electron transfer steps involving aggregates of four V$^{2+}$ ions[3,4] or pairs of V$_2^{2+}$ ions.[7]

Employing butadiene-1,3 as the substrate, we have found that it is reduced exclusively to butene-1; neither *n*-butane nor butenes-2 formed under the conditions of N$_2$ reduction, indicating that the two-electron reduction product is favored and that no isomerization occurs (see Table I). We subsequently became interested in the reactions of V(OH)$_2$ with various alkylating agents. With simple alkyl halides, *alkanes* are formed by way of reductive dehalogenation; these reactions occur without the formation of new C–C bonds. Hydrocarbons that could have arisen from the coupling of two alkyl radicals were not observed. Approximate relative rates of alkane production from various alkyl halides are given in Table I together with the results of experiments with other substrates. Scheme II summarizes the most important reactions observed. It may be seen that diazirine is reduced to diaziridine just as dimethyldiazene is reduced to *s*-dimethylhydrazine. On heating, further reduction of diaziridine to formaldehyde and ammonia was observed, while *s*-dimethylhydrazine is reduced to methylamine. Diazomethane reacts with V(OH)$_2$–Mg(OH)$_2$ rapidly to yield N$_2$ and ch$_4$. Carbon monoxide is not reduced and acts as an inhibitor of the reduction of N$_2$ and of other

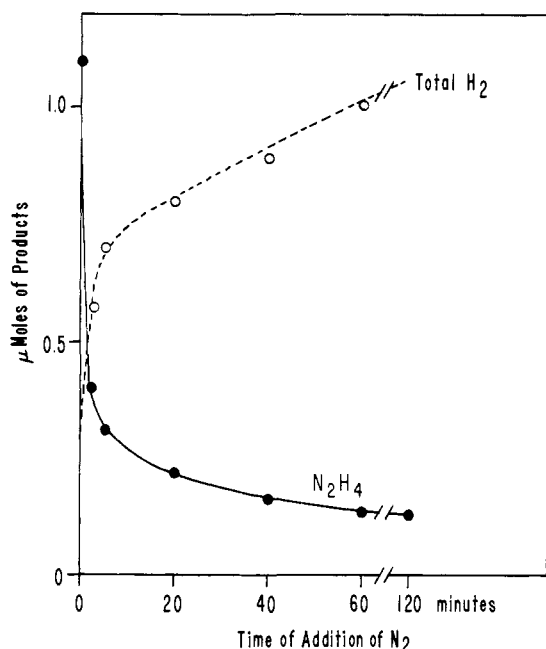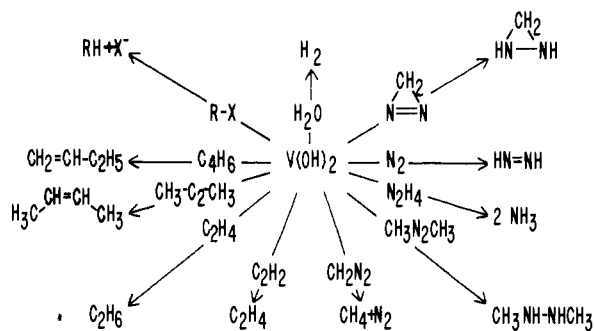Scheme I. Reduction of N$_2$ in the V(OH)$_2$–Mg(OH)$_2$ System
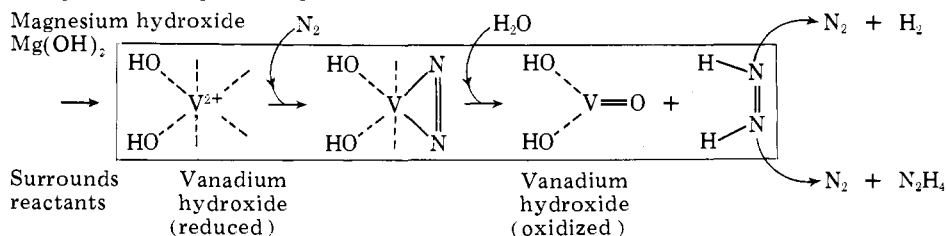
**Figure 1.** Yields of $N_2H_4$ from experiments in which $V(OH)_2$-$Mg(OH)_2$ gels were generated under argon and brought into contact with $N_2$ at 1 atm after the times indicated. Suspensions consisted of 40 $\mu$mol of $V(OH)_2$ and 2000 $\mu$mol of $Mg(OH)_2$ in a total solution volume of 11 mL.

**Scheme II.** Some Reactions in the $V(OH)_2$-$Mg(OH)_2$ System



**Table I.** Reactions of $V(OH)_2$-$Mg(OH)_2$ with Various Substrates[a]

| Substrate | Product(s) | Rel rate[b] | Ref |
|---|---|---|---|
| $N_2$ | $(N_2H_2)$,$N_2H_4$.$(H_2)$ | 100 | 1 |
| $C_2H_2$ | $C_2H_4$ | 73 | 1 |
| $C_2H_4$ | $C_2H_6$ | 12.5 | This work |
| $C_3H_6$ | $C_3H_8$ | 2.8 | This work |
| 1,3-$C_4H_6$ | 1-$C_4H_6$ | 1.5 | This work |
| $H_2O$ | $H_2$ | 0.3 | This work |
| $CH_3Cl$ | $CH_4$ | 0.7 | This work |
| $C_2H_5Cl$ | $C_2H_6$ | 0.9 | This work |
| $n$-$C_3H_7Cl$ | $C_3H_8$ | 0.33 | This work |
| $i$-$C_3H_7Cl$ | $C_3H_8$ | 0.09 | This work |
| $n$-$C_4H_9Cl$ | $C_4H_{10}$ | 0.6 | This work |
| 2-$C_4H_9Cl$ | $C_4H_{10}$ | 0.03 | This work |
| $t$-$C_4H_9Cl$ | $C_4H_{10}$ | ~0.01 | This work |
| $C_5H_{11}Cl$ (neopentyl) | $C_5H_{12}$ (neopentane) | ~0.05 | This work |
| $C_3H_7Br$ | $C_3H_8$ | 1.0 | This work |
| $C_3H_7I$ | $C_3H_8$ | 5.0 | This work |
| $CH_2N_2$ | $CH_4$,$N_2$ | N.D. | This work |
| $CH_3N$=$NCH_3$ | $CH_3NHNHCH_3$. $CH_3NH_2$ | N.D. | This work |
| $CH_2N_2$ (diazirine) | $CH_2N_2H_2$ (diaziridine), $CH_2$=O, $2NH_3$ | | This work |
| | | N.D. | This work |
| $CN^-$ | $CH_2$=O, $NH_3$ | Slow | This work |

[a] Under standard reaction conditions outlined in the Experimental Section, at 25 °C. [b] Approximate values, based on initial rates of $N_2$ reduction at 1 atm.

substrates as will be described below. Carbon monoxide also was found to *stimulate* $H_2$ *production*. A similar effect was observed with $CN^-$, which is itself slowly reduced to $CH_2$=O and $NH_3$.

**Reduction of Nitrogen.** A key feature of the reactions of $N_2$ with $V(OH)_2$ is that appreciable amounts of $N_2H_4$ are only formed if the $V(OH)_2$ is incorporated into inert host lattices such as $Mg(OH)_2$ or $ZrO_2$·aq. Although $N_2$ is also reduced by suspensions of $V(OH)_2$ as such, only traces of $N_2H_4$ are formed while $H_2$ production is noticeably *stimulated*. This remarkable phenomenon was attributed to the intermediate formation and subsequent base-catalyzed decomposition of $N_2H_2$ into the elements.[1] It is obviously necessary to incorporate the $V^{2+}$ ions into the $Mg(OH)_2$ lattice in order to provide a protecting environment for the $N_2H_2$. Since the $Mg(OH)_2$ lattice has only a finite capacity to hold $N_2H_2$ within the confinements of its polymeric layer structure it is not surprising that the yields of $N_2H_4$ depend critically on the $V^{2+}$: $Mg^{2+}$ ratio, the $N_2$ pressure, and details of the manner in which the $V(OH)_2$-$Mg(OH)_2$ gels are generated. Since the reaction system is heterogeneous and involves a sparingly soluble gaseous substrate, even the surface area of gel which is allowed to come into contact with $N_2$ has an effect on the yields of $N_2H_4$. Accordingly, all experiments must be performed under strictly identical conditions if they are to be

compared with each other, which includes the use of reaction vessels of identical shape and capacity. The reaction is furthermore kinetically complex because of aging phenomena of the $V(OH)_2$-$Mg(OH)_2$ gels which influence the rates of diffusion of gaseous substrates. Figure 1 shows the results of experiments in which $V(OH)_2$-$Mg(OH)_2$ gels were generated under argon and substrate $N_2$ was introduced at later time points. It may be seen that the yields of $N_2H_4$ decline to about one-half of the original amount within 20 min, a fact which we attribute to aging phenomena. However, these experiments also demonstrate that $N_2$ genuinely diffuses through the $Mg(OH)_2$ host lattice, which is remarkable considering the very high concentration of alkali (6 N KOH !) used to generate the gels.

The highest yields of $N_2H_4$ are observed if the $V(OH)_2$-$Mg(OH)_2$ gels are generated not in aqueous KOH, but instead in the presence of 5–20% of an alcohol, usually $CH_3OH$. Higher monohydric alcohols still increase the yields of $N_2H_4$ relative to runs in purely aqueous medium but are as a rule less effective than $CH_3OH$.[8] The stimulatory effects of alcohols on product yields are also observed with $C_2H_2$ as the substrate (Figure 2, Table II). Interesting structure-related effects were noted upon addition of polyhydric alcohols. With propanediol-2,3, the reactivity of the gels was high with respect to both $N_2$ and $C_2H_2$; it was very low with propanediol-1,3, however (Table II). In view of these observations the number of additives studied was increased to include ethylenediamine, propylenediamine, ethanolamine, and other compounds, including two detergents (Triton and SDS). The effects of *ethanolamine* were investigated in greater detail and are presented in Figures 3 and 4. Ethanolamine causes an increase of the yields of $N_2H_4$ and diminution of $H_2$ production, for reasons to be discussed below.

**Inhibition of $N_2$ Reduction by, CO, $CN_2^-$ and $C_2H_2$.** Carbon monoxide was previously[9] described as a weak inhibitor of $N_2$ reduction in the $V(OH)_2$-$Mg(OH)_2$ system but was found under our reaction conditions to inhibit $N_2H_4$ production quite significantly and with concomitant *stimulation* of $H_2$

**Table II.** Effects of Additives on the Reduction of $N_2$ and of $C_2H_2$ by Alkaline Suspensions of $V(OH)_2$-$Mg(OH)_2$ at 1 atm of Pressure and 25 °C[a]
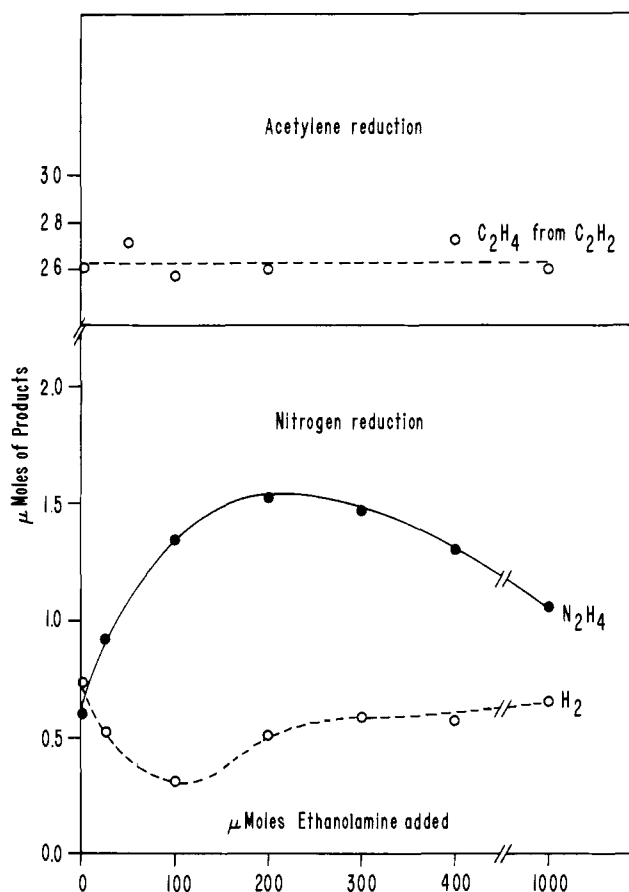
| Additive | Amount added | N₂ redn (yields, μmol) N₂H₄ | H₂ | N₂H₄/H₂ | C₂H₂ redn (yields, μmol) C₂H₄ |
|---|---|---|---|---|---|
| None | | 0.45 | 0.22 | 2.05 | 10.9 |
| CH₃OH | 18% vol | 1.15 | 0.50 | 2.3 | 24.7 |
| C₂H₅OH | 18% vol | 1.05 | 0.25 | 4.2 | 25.0 |
| n-C₃H₇OH | 18% vol | 0.72 | 0.22 | 3.3 | 25.4 |
| n-C₄H₉OH | 18% vol | 0.64 | 0.22 | 2.9 | 26.4 |
| i-C₄H₉OH | 18% vol | 0.51 | 0.44 | 1.2 | 23.8 |
| t-C₄H₉OH | 18% vol | 1.04 | 0.35 | 3.0 | 27.0 |
| c-C₆H₁₁OH | 18% vol | 0.01 | 0.01 | 1.0 | 1.4 |
| HOCH₂CH₂OH | 18% vol | 0.74 | 0.25 | 3.0 | 22.4 |
| HOCH(CH₃)CH₂OH | 18% vol | 0.87 | 0.40 | 2.2 | 24.6 |
| HO(CH₂)₃OH | 18% vol | 0.03 | 0.07 | 0.43 | 11.8 |
| HO(CH₂)₄OH | 18% vol | 0.09 | 0.26 | 0.35 | 14.2 |
| HOCH₂CH(OH)CH₂OH | 18% vol | 0.04 | 0.15 | 0.27 | 13.5 |
| C₆H₅OH | 1.2% wt | 0.62 | 0.44 | 1.36 | 16.9 |
| 1,2-C₆H₄(OH)₂ | 6.0% wt | 0.03 | 0.03 | 1.00 | 14.1 |
| Triton X-100 | ~0.6 mmol | 0.10 | 0.03 | 3.3 | 22.7 |
| SDS | 0.6 mmol | 0.85 | 0.25 | 3.4 | 22.7 |
| HOCH₂CH₂NH[b] | 0.2 mmol | 1.86 | 0.40 | 4.7 | 24.5 |
| H₂NCH₂CH₂NH[b] | 0.2 mmol | 1.82 | 0.40 | 4.5 | 24.5 |
| H₂N(CH₂)₃NH₂[b] | 0.2 mmol | 1.84 | 0.33 | 5.6 | 24.5 |

[a] Yields measured after 20 min. The $V(OH)_2$-$Mg(OH)_2$ gels were generated from 40 μmol of $V^{2+}$ (aq) and 2000 μmol of $Mg^{2+}$, respectively; all additives were added to the reaction mixture before gel formation except where indicated. [b] Added 60 s after gels had been generated.
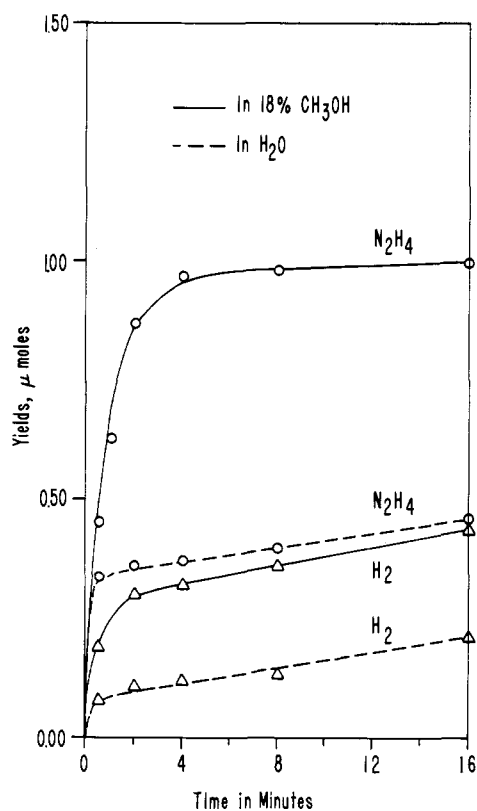


**Figure 2.** Time dependence of $N_2$ reduction by suspensions of $V(OH)_2$-$Mg(OH)_2$ generated in the absence and presence of 18 vol % of $CH_3OH$. Gels contained 40 μmol of $V(OH)_2$ in 2000 μmol of $Mg(OH)_2$: reaction temperature 25 °C.



**Figure 3.** Effect of ethanolamine on the yields of $N_2H_4$ and $H_2$ in the reduction of $N_2$ at 1 atm of pressure. Increasing amounts of ethanolamine were added 60 s after precipitation of the gels; yields of products were measured after 20 min of reaction at 25 °C.

formation. The evolution of $H_2$ reached a maximum rate at CO pressures of about 0.2 atm and declined at higher pressures. However, it is still quite rapid at 1 atm (see Figure 5). Added $CN^-$ (after the hydroxide gel had been generated, to avoid formation of soluble cyano complexes of vanadium!) also lowered the yields of $N_2H_4$ and stimulated $H_2$ production. With $C_2H_2$, $N_2$ reduction was inhibited without a stimulation

of $H_2$ formation; $C_2H_2$ is rapidly reduced under these conditions.

**Inhibition of $N_2$- and $C_2H_2$ Reduction by Alkanes and $H_2$.** The use of *alkanes* as inhibitors of substrate reduction in the
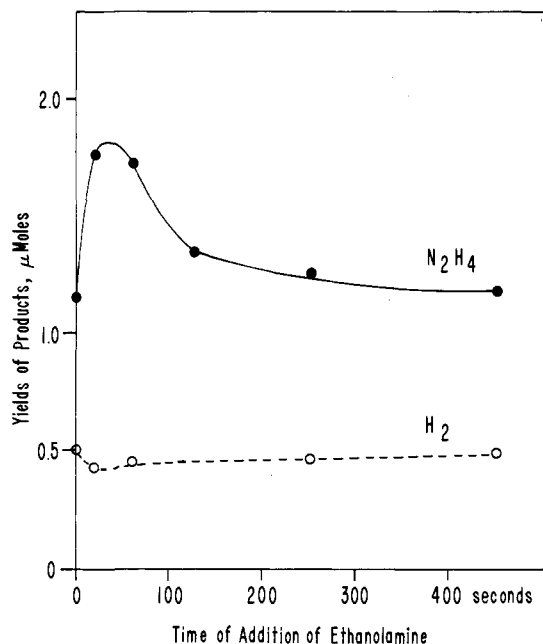
**Figure 4.** Effect of the addition of 50 $\mu$mol of ethanolamine to reacting suspensions of $V(OH)_2$-$Mg(OH)_2$ under 1 atm of $N_2$ as a function of time. Overall yields measured after 20 min of reaction at 25 °C.
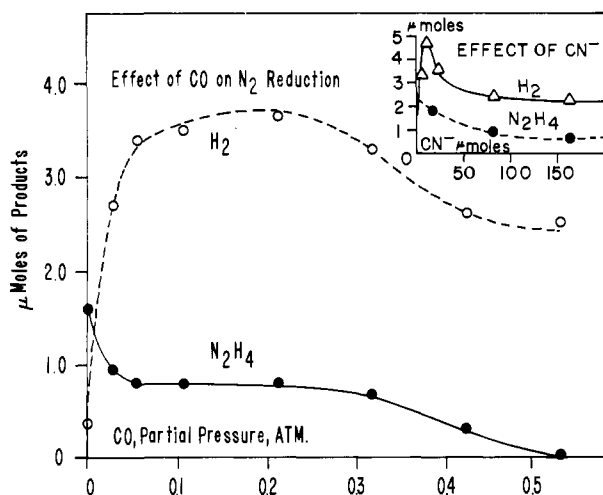


**Figure 5.** Effect of increasing concentrations of CO in the gas phase on the yields of $N_2H_4$ and $H_2$ in $N_2$-fixation experiments at 1 atm and 25 °C. The $V(OH)_2$-$Mg(OH)_2$ gels were generated from 40 $\mu$mol of $V^{2+}$ (aq) and 2000 $\mu$mol of $Mg^{2+}$ in $H_2O$ containing 18 vol % of $CH_3OH$.



**Figure 6.** Effects of alkanes on the yields of $N_2H_4$ and $H_2$ in $N_2$-fixation experiments at $p_{N_2}$ = 1 atm. All hydrocarbons were present at 0.3 atm in the gas phase or the equivalent liquid volumes at $t$ = 0. Yields were determined after 20 min of reaction at 25 °C.



**Figure 7.** Effects of alkanes on the yields of $C_2H_4$ and $C_2H_2$ on reduction with $V(OH)_2$-$Mg(OH)_2$. Reaction conditions as outlined in legend of Figure 6.

$V(OH)_2$-$Mg(OH)_2$ system was contemplated in order to obtain information on factors which influence the diffusion of $N_2$ through the $Mg(OH)_2$ lattice. Figure 6 shows that the reduction of $N_2$ to $N_2H_4$ is inhibited significantly by $C_2H_6$ and $C_3H_8$ but only weakly by $CH_4$, $n$-$C_4H_{10}$, and higher $n$-alkanes. In the course of these experiments the evolution of $H_2$ was monitored as well; the observed yields are included in Figure 6. It may be seen that $C_2H_6$ inhibits $N_2$ reduction but *stimulates* the evolution of $H_2$. The effect on the $H_2$ evolution is $N_2$ dependent and not observed under argon or $C_2H_2$. On the other hand, $C_3H_8$ inhibits both $N_2$ reduction and $H_2$ formation. The reduction of $C_2H_2$ is also inhibited by small hydrocarbons; among simple alkanes tested, $C_2H_6$ was the most potent inhibitor (Figure 7). Since $H_2$ is a competitive inhibitor of $N_2$ reduction by nitrogenase we also explored its effect on $N_2$ reduction in the present system. Only a 20% diminution of the yield of $N_2H_4$ was observed when the reduction of $N_2$ at 1 atm of pressure was performed in the presence of 0.5 atm of $H_2$.
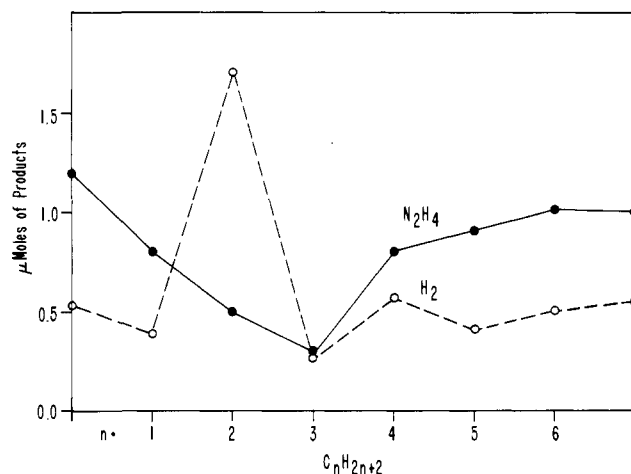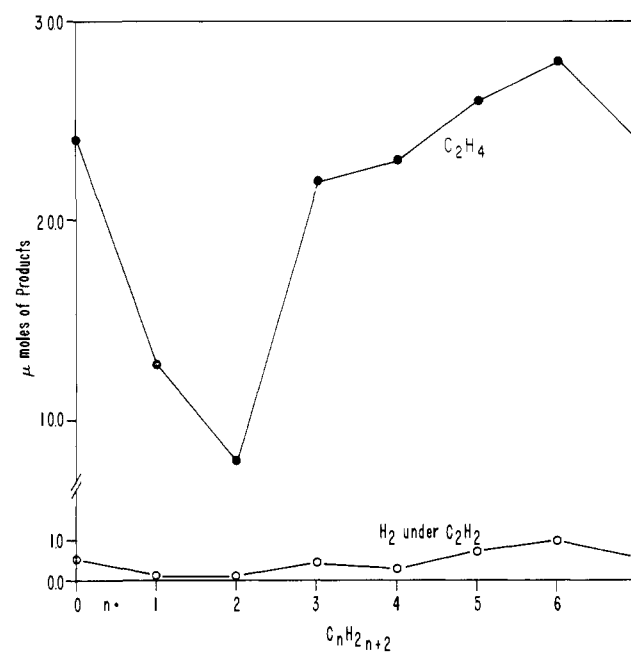
**Deuterium Isotope Effects.** The evolution of $D_2$ from suspensions of $V(OD)_2$-$Mg(OD)_2$ in alkaline $D_2O$ occurs at approximately $\frac{1}{3}$ of the rate of the corresponding reaction in $H_2O$. However, neither the reduction of $C_2H_2$ nor of $C_2H_4$ or $C_3H_6$ shows a similarly large kinetic H–D effect. Although the rates of product formation are diminished in $D_2O$ relative to $H_2O$, the H–D effect is small and somewhat erratic, particularly in early phases of the reaction, suggesting that differences in the rates of aging of the gels in $H_2O$ and $D_2O$ are responsible and will hence not be described in detail. The reduction of $N_2$ to $N_2H_4$ occurs at a slightly faster initial rate than the reduction of $N_2$ to $N_2D_4$, but the terminal yields are almost identical. However, 1.5 times more $H_2$ and $D_2$ is formed, as follows from Table III.

**Dependence of $H_2$ and $N_2H_4$ Yields on $N_2$ Pressure.** The rates of $H_2$ evolution from $V(OH)_2$-$Mg(OH)_2$ suspensions are dependent on the partial pressure of $N_2$ and the concentration of $V^{2+}$ in the gels. At concentrations of 10 $\mu$mol of $V^{2+}$ per

**Table III.** Product Yields and Ratios from the Reduction of $N_2$ in $H_2O$ and $D_2O^a$

| Reaction time, s | $H_2$ $(D_2)$, $\mu$mol | $H_2/D_2$ | $N_2H_4$ $(N_2D_4)$, $\mu$mol | $N_2H_4/N_2D_4$ | Reducing equiv consumed $\mu$mol $H_2O$ $(D_2O)$ | Ratio |
|---|---|---|---|---|---|---|
| 28 | 0.38 (0.24) | 1.58 | 0.50 (0.42) | 1.19 | 2.76 (2.16) | 1.28 |
| 38 | 0.43 (0.26) | 1.65 | 0.69 (0.56) | 1.23 | 3.62 (2.74) | 1.32 |
| 53 | 0.46 (0.28) | 1.64 | 0.82 (0.84) | 0.98 | 4.20 (3.92) | 1.07 |
| 75 | 0.48 (0.32) | 1.50 | 0.94 (0.99) | 0.95 | 4.72 (4.60) | 1.02 |
| 1200 | 0.70 (0.50) | 1.40 | 1.00 (1.06) | 0.94 | 5.40 (5.24) | 1.03 |

$^a$ From gels containing 40 $\mu$mol of $V^{2+}$ per 2000 $\mu$mol of $Mg(OH)_2$ or $Mg(OD)_2$, respectively.

**Table IV.** Observed $H_2/N_2H_4$ Ratios at 1 atm of $N_2$ as a Function of the $V^{2+}$ Concentration in the $Mg(OH)_2$ Gels

| | $V^{2+}$ concn, $\mu$mol$^a$ | | | |
|---|---|---|---|---|
| | 10 | 20 | 30 | 40 |
| $H_2/N_2H_4$ ratios after 45 min of reaction | 2.5 | 1.15 | 0.56 | 0.403 |

$^a$ In 2000 $\mu$mol of $Mg(OH)_2$.

2000 $\mu$mol of $Mg(OH)_2$, more $H_2$ than $N_2H_4$ is formed even at 1 atm of $N_2$; as the $V^{2+}$ concentration is increased, the $H_2/N_2H_4$ ratios begin to reflect the decline in $H_2$ and the increase in $N_2H_4$ production (Table IV).

The dependence of the rates of $H_2$ production on the partial pressure of nitrogen is nonlinear; the rates reach a maximum at intermediate $N_2$ pressures which shifts as a function of time. This is shown in Figure 8 for the $V^{2+}$ concentration of 40 mol per 2000 mol of $Mg(OH)_2$. The yields of $N_2H_4$ under these conditions exhibit a clearly *linear dependence on* $p_{N_2}{}^2$ (Figure 9).
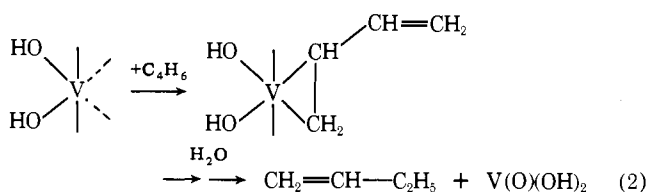
**Discussion**

**Reduction of Substrates Other Than $N_2$.** The present study demonstrates that $V(OH)_2$ behaves as a two-electron reductant even in reactions with substrates that can accept more than two electrons. At high partial pressures, acetylene is reduced exclusively to ethylene, in yields consistent with the stoichiometry of reaction eq 1.[1] At low partial pressures $C_2H_2$ is reduced to

$$HO\diagdown \quad \underset{\text{(rate)}}{\overset{+C_2H_2}{\longrightarrow}} \quad HO\diagdown CH$$

$$\xrightarrow[\text{(fast)}]{H_2O} \quad C_2H_4 \;+\; V(O)(OH)_2 \quad (1)$$
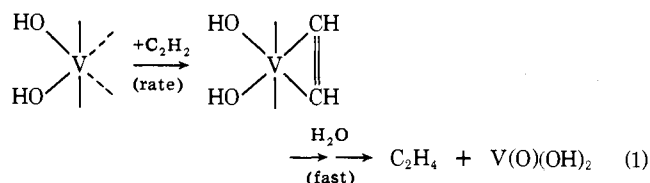
a mixture of $C_2H_4$ and $C_2H_6$ owing to a secondary reaction of product $C_2H_4$ with the V(II) reductant. The side-on interaction of $C_2H_2$ with $V^{2+}$ is supported by the observed exclusive reduction of butyne-2 to *cis*-butene-2,[1] and confirmed by the formation of *cis*-$C_2H_2D_2$ from $C_2H_2$ in $D_2O$, first demonstrated in the present paper.

Even with butadiene-1,3, only a two-electron reduction product, butene-1, is formed; the reaction is formulated in eq 2. The four-electron reduction product, *n*-butane, was not
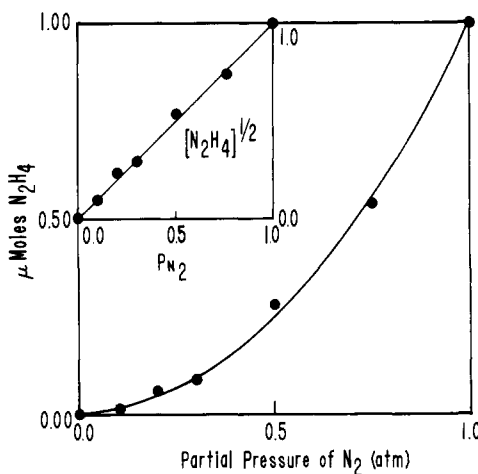
$$HO\diagdown \quad \overset{+C_4H_6}{\longrightarrow} \quad HO\diagdown CH \diagdown CH{=}CH_2$$

$$\xrightarrow{H_2O} \quad CH_2{=}CH{-}C_2H_5 \;+\; V(O)(OH)_2 \quad (2)$$

observed, indicating that a concerted reduction of $C_4H_6$ at two adjacent $V^{2+}$ centers is not favored.

The reaction of $V(OH)_2$ with *alkyl halides* may be plausibly
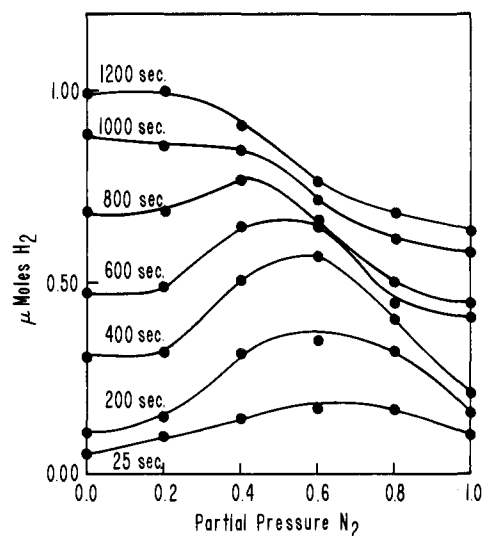


**Figure 8.** Evolution of $H_2$ from $V(OH)_2$–$Mg(OH)_2$ suspensions as a function of $p_{N_2}$ and reaction time. Suspensions contained 40 $\mu$mol of $V(OH)_2$ per 2000 $\mu$mol of $Mg(OH)_2$.



**Figure 9.** Dependence of the yields of $N_2H_4$ on $p_{N_2}$. Reaction conditions as given in the legend to Figure 8. Solid line shows calculated dependence on $p_{N_2}{}^2$; insert is a plot of $[N_2H_4]^{1/2}$ vs. $p_{N_2}$, demonstrating the second-order dependence of the yields of $N_2H_4$ on $N_2$.

assumed to occur by way of a nucleophilic displacement of halide ion and organovanadium species undergoing further reaction in terms of reaction 3. The nucleophilic reactivity of

$$HO\diagdown \quad \underset{-X^-}{\overset{+RX}{\longrightarrow}} \quad HO\diagdown R \quad \overset{+H_2O}{\longrightarrow} \quad V(O)(OH)_2 \;+\; RH \quad (3)$$
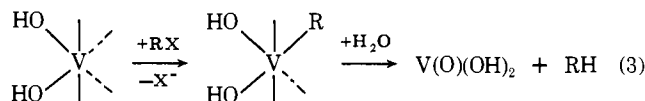
$V(OH)_2$ must be considerable as relatively unreactive *secondary* and *tertiary* alkyl chlorides are dehalogenated at measurable rates (see Table I). A quantitative estimate of the
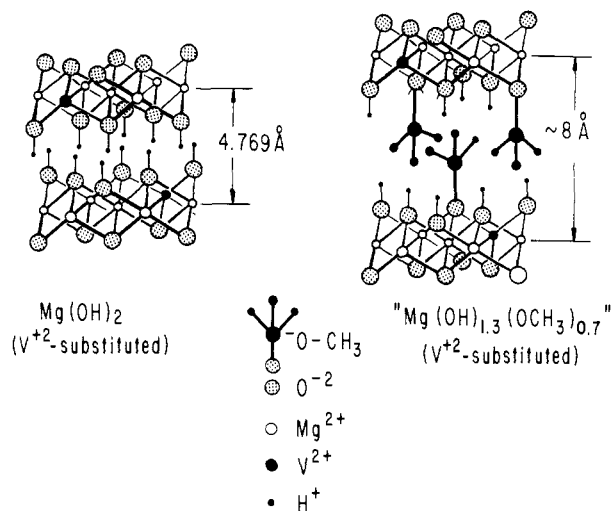
Figure 10. Sections of isomorphously $V^{2+}$-substituted $CdI_2$-type layer structures of $Mg(OH)_2$ (Brucite) and of the phase "$Mg(OH)_{1.3}$-$(OCH_3)_{0.7}$", demonstrating the increase of the $d_{001}$ interlayer distance as reported in ref 13. Note how the substitution of $OH^-$ by $CH_3O^-$ introduces hydrophobic regions in the interlayer spacings.

nucleophilic reactivity constant was not attempted since the rates in Table I are composite numbers and somewhat atypical for SN2 reactions.[10] The reaction of $V(OH)_2-Mg(OH)_2$ with *diazomethane* yielded methane and nitrogen and is formulated in eq 4. While diimide is not reduced by $V^{2+}$ because of its
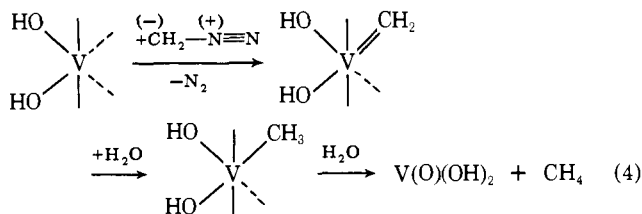


thermodynamic instability and short lifetime in solution, diazirine and dimethyldiazene are reduced; the reactions are exemplified in eq 5 for diazirine.
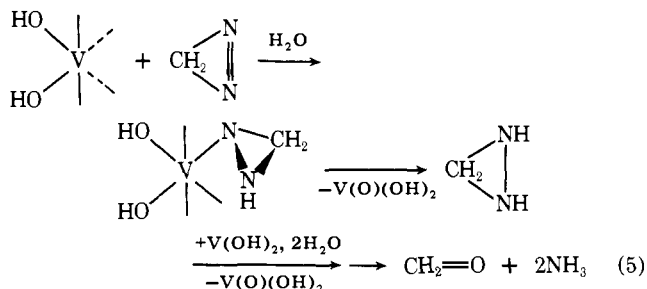


**Hydrogen Evolution.** The substrate-*independent* $H_2$ evolution from aqueous suspensions of $V(OH)_2$ may be assumed to occur via an intermediate vanadium hydride which could also be regarded as the Brønsted acid of the $V^{2+}$ nucleophile. The reaction is formulated in eq 6. The rates of $H_2$ evolution from
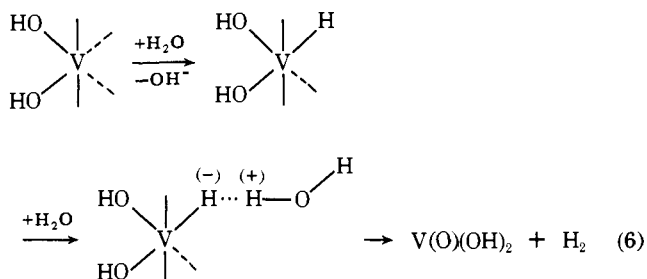


$V(OH)_2$ *incorporated* into $Mg(OH)_2$ are substantially slower, suggesting that the effective concentration of $H_2O$ inside the $Mg(OH)_2$ lattice is lower than in the outside medium.

**Reduction of Nitrogen. Role of the $Mg(OH)_2$ Host Lattice.** The observed $N_2$-*stimulated* evolution of $H_2$ from suspensions of $V(OH)_2$ in the absence of $Mg(OH)_2$ led us to propose that the $Mg(OH)_2$ host lattice provides an environment in which $N_2H_2$, the first product of $N_2$ reduction, is protected against base-catalyzed decomposition into $N_2 + H_2$, which occurs rapidly whenever diimide is generated outside the host lattice in alkaline media.[1] An examination of the polymeric layer structure of $Mg(OH)_2$ (see Figure 10) reveals that the inside of the $Mg(OH)_2$ lattice may be regarded as a *buffered region* in which the effective concentration of $OH^-$ is significantly lower than in the alkaline dispersion medium.[11] This also follows from the fact that $Mg(OH)_2$ may be precipitated from strongly alkaline aqueous solutions without significant occlusion of alkali hydroxide.

In spite of its apparent low affinity for foreign inorganic anions or cations, the $Mg(OH)_2$ lattice is readily penetrated by a wide variety of covalent molecules, including short-chain alkanes, alkenes, and alkynes. This permeability is enhanced if the $Mg(OH)_2$ is precipitated from solutions containing alcohols, which may be assumed to be incorporated in the manner shown in Figure 10. Thus, it is known that brucite reacts with $CH_3OH$ on heating under pressure to produce mixed methoxy hydroxides among which a phase "$Mg(OH)_{1.3}(OCH_3)_{0.7}$" has been characterized.[12] This phase possesses a brucite-like $CdI_2$ layer structure in which the interlayer distance $d_{001}$ is increased from 4.769 to about 8.0 Å. Such expansion of the interlayer distance could also occur in the $V(OH)_2-Mg(OH)_2$ gels precipitated from aqueous-alcoholic media. It has the remarkable effect of introducing hydrophobic regions in the interlayer area besides rendering the lattice more permeable to covalent reactants. Accordingly, alkoxide-containing precipitates of $V(OH)_2-Mg(OH)_2$ are expected to react with $N_2$ more rapidly than those generated from purely aqueous media. However, the reactivity of the gels also depends on the structure of the alcoholic additives as will be discussed in the next section.

**Effects of Additives.** Figure 2 shows that the reduction of $N_2$ with *aqueous* alkaline suspensions of $V(OH)_2-Mg(OH)_2$ proceeds rapidly only during a brief phase of the reaction in which the gel remains in a state of enhanced permeability. Already after 30 s of reaction the rates of $N_2H_4$ and $H_2$ production drop to about $1/30$ of the initial rates. In the presence of $CH_3OH$, the $V(OH)_2-Mg(OH)_2$ gels retain their initial high reactivity for significantly longer periods with attendant increases in the yields of both $N_2H_4$ and $H_2$. Table II indicates how the yields of both products are influenced by a variety of other organic additives. It may be seen, for example, that the yields of $N_2H_4$ and of $H_2$ decline in the sequence $CH_3OH >$ $C_2H_5OH > n$-$C_3H_7OH > n$-$C_4H_9OH$, while the ratios of $N_2H_4$:$H_2$ reach a maximum in the presence of $C_2H_5OH$. Compared to $n$-$C_4H_9OH$, $i$-$C_4H_9OH$ produces more than twice the amount of $H_2$, while $t$-$C_4H_9OH$ affords higher absolute yields of $N_2H_4$ at a slightly increased $N_2H_4$:$H_2$ ratio. Cyclohexanol, however, causes a sharp drop of the amount of $N_2H_4$ produced and *increases* the $H_2$ production. With the exception of cyclohexanol, these aliphatic alcohols do not markedly affect $C_2H_2$ reduction. Although the yields of $C_2H_4$ are more than twice as high as those observed in pure aqueous systems of $V(OH)_2-Mg(OH)_2$, all these alcohols cause approximately the same amount of stimulation. On the other hand, the inhibitory effect of cyclohexanol is observed for $N_2$ *and* $C_2H_2$ as the substrate. Obviously, some organic additives modify the structure of the host lattice to affect mainly the reactions involving $N_2H_2$, while other additives may be assumed to "clog up" the gels, an effect which can be noticed for

$N_2$ and $C_2H_2$ as it prevents the access of substrates to the $V^{2+}$ sites. Gel "clogging" is the more frequently observed and stronger phenomenon. This follows from a statistical correlation of the data shown in Table II. The yields of $N_2H_4$ from $N_2$, and those of $C_2H_4$ from $C_2H_2$, correlate directly, with $r = 0.66$ ($P = 0.001$), where $r$ is the calculated linear correlation coefficient. Gel "clogging" was also observed with one of the two detergents studied, i.e., with Triton X, which consists of a mixture of alkylphenoxypolyglycols. Its inhibitory effect may be related to that of propanediol-1,3. The other detergent, SDS (sodium dodecyl sulfate), is only a weak inhibitor, presumably because it is not incorporated (see Table II).

**Inhibition by Alkanes.** The observed inhibitory effects of short-chain alkanes in the reduction of $N_2$ and $C_2H_2$ demonstrates that the $V^{2+}$-doped $Mg(OH)_2$ possesses the properties of a *molecular sieve*. Whereas $CH_4$ and $n$-$C_4H_{10}$ inhibit $N_2$ reduction only slightly, $C_2H_6$ and $C_3H_8$ are strong inhibitors. Similar inhibitory effects of alkanes are also observed with $C_2H_2$ as the substrate. However, while short-chain hydrocarbons inhibit $C_2H_2$ reduction and $H_2$ evolution, $N_2$ reduction is inhibited by $C_2H_6$ with a concomitant *stimulation of $H_2$ production*. With $C_3H_8$, $N_2$ reduction and $H_2$ formation are both inhibited (see Figures 6 and 7). The anomalous effect of $C_2H_6$ on $H_2$ production as compared to $C_3H_8$ is interpreted as follows: $C_2H_6$ apparently can enter the $Mg(OH)_2$ lattice and lowers the effective concentration of $N_2$. Accordingly, less $N_2H_2$ is generated and a greater proportion decomposes into the elements; the net result is enhanced, $N_2$-dependent $H_2$ production. $C_3H_8$, in contrast, has a stronger "clogging" effect than $C_2H_6$ and prevents $N_2$ from reaching the $V^{2+}$ sites. Hence, little $N_2H_4$ or $H_2$ is produced.

**Effects of Ethanolamine and of Alkyldiamines.** Ethylenediamine, diaminopropane-1,3, and ethanolamine belong to a special group of additives which cause a significant stimulation of the yields of $N_2H_4$ when added in optimal amounts to *reacting* $V(OH)_2$-$Mg(OH)_2$ gels with $N_2$ as the substrate. In the presence of these additives, the lowest relative yields of $H_2$ are produced (see Table II and Figures 3 and 4). These bases appear to protect $N_2H_2$ from base-induced decomposition into the elements. Hünig et al.[13] reported that $N_2H_2$ generated from sulfonyl hydrazides similarly did not undergo base-catalyzed decomposition into $N_2$ and $H_2$ if *ethanolamine* rather than KOH was employed as the base in the reaction

$$RSO_2NHNH_2 \xrightarrow[-BH^+, \ -RSO_2^-]{+B} [NH{=}NH] \qquad (7)$$
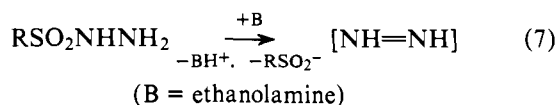
$$(B = ethanolamine)$$

With KOH as the base, decomposition of $N_2H_2$ into $N_2$ and $H_2$ was virtually quantitative.[13] Our results show that ethanolamine and a number of alkylenediamines also protect $N_2H_2$ from decomposition in the $V(OH)_2$-$Mg(OH)_2$ system. It is noteworthy that these amines have no effect on $C_2H_2$ reduction and that they are most effective if employed *after* the gels were already generated. The alcoholic additives, in contrast, must be added to the reaction solutions *prior* to the precipitation of the gels to show their effects.

**Effects of Inhibitors.** The inhibition of $N_2$ reduction by CO is of interest as it is accompanied by a *stimulation* of $H_2$ production. Cyanide exhibits the same qualitative behavior, but acetylene inhibits $N_2$ reduction and lowers $H_2$ production. Carbon monoxide may be plausibly assumed to interact with the $V^{2+}$ centers; at low partial pressures one coordination site will be blocked, preventing the side-on interaction of $N_2$ without interfering with $H_2$ evolution. At high partial pressures of CO, additional coordination sites on $V^{2+}$ may become occupied, leading to inhibition of $H_2$ production, as indicated in Scheme III. The effects of cyanide are explained analogously. Scheme III is similar to one proposed in 1971, describing the

Scheme III. Stimulation of $H_2$ Production by Carbon Monoxide
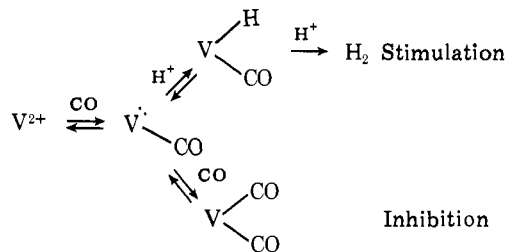


CO effect in molybdothiol model systems of nitrogenase.[14]

**Mechanism of $N_2$ Reduction. New Evidence for Diimide.** The diimide mechanism of $N_2$ reduction by $V(OH)_2$-$Mg(OH)_2$ is supported by the observed accumulation of a reactive species in early phases of the reaction which subsequently disappears by way of a second-order reaction.[1] Further confirmatory evidence was provided by the observed $N_2$-stimulated production of 1-propanol from allyl alcohol under the reaction conditions[15] and the $N_2$ stimulation of $H_2$ formation from suspensions of $V(OH)_2$ in the absence of the $Mg(OH)_2$ host lattice.[1] The mechanism is now also supported by the observed dependence of the $N_2H_4$ yields on $p_{N_2}^2$ (see Figure 9), which essentially rules out any mechanism invoking the direct reduction of $N_2$ to $N_2H_4$. The fact that the reaction is so cleanly of second order in $N_2$ is probably fortuitous as some of the $N_2H_2$ decomposes into $N_2$ and $H_2$. However, deviations of the dependence of the yields of $N_2H_4$ on $p_{N_2}^2$ due to this reaction would be noticeable mainly at low partial pressures of $N_2$. On the other hand, the dependence of the yields of $H_2$ on the partial pressure of $N_2$ as exemplified in Figure 8 illustrates the complexity of the system. The anomalous stimulation of $H_2$ production at low partial pressures of $N_2$ is clearly indicative of $N_2H_2$ decomposition, which is favored over the disproportionation if it is generated in low initial or stationary concentrations; the same conclusion may be drawn from the data given in Table IV. The mechanism of $N_2$ reduction as formulated in eq 8 includes the



$$(8)$$
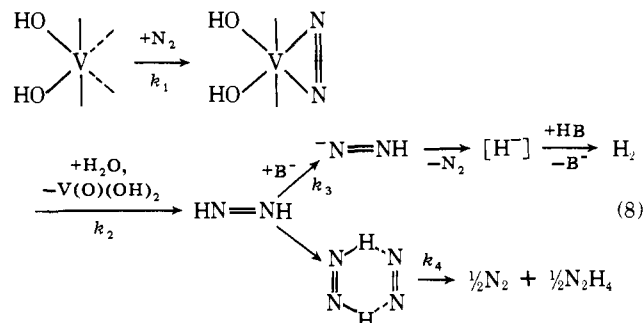
competing decomposition of $N_2H_2$ which is base catalyzed and which can be in part eliminated by the addition of $N_2H_2$-stabilizing bases such as ethanolamine. Since $V(OH)_2$-$Mg(OH)_2$ reduces 2-butyne to *cis*-2-butene and, as we have now established, $C_2H_2$ in $D_2O$ to *cis*-1,2-$C_2H_2D_2$, we postulate that *cis*-$N_2H_2$ is generated on hydrolysis of the reactive vanadium nitride intermediate.

The kinetic H–D isotope effect on diimide disproportionation ($k_4$ in eq 8) may be estimated from the data in Table III as approximately 2.25, and that of diimide decomposition as about 1.5, if the assumption is made that all of the $H_2$ or $D_2$ generated arises from the decomposition of diimide. The latter condition is probably best fulfilled during the early phases of the reaction. Since the kinetic H–D effects of reduction of $C_2H_2$, $C_2H_4$, or $C_3H_6$ are close to unity, we conclude that the hydrolysis of the vanadium–substrate complexes is not rate determining. The reduction of these organic substrates furthermore occurs even in the absence of the $Mg(OH)_2$ host lattice, as the olefinic or paraffinic reaction products are alkali

stable. The requirement of a protecting host lattice in the reduction of $N_2$ by $V(OH)_2$ thus is in itself a proof for the intermediacy of diimide. In view of the similarity of the mechanism of $N_2$ reduction, the $V(OH)_2$-$Mg(OH)_2$ system may hence be regarded as a stoichiometric *analogue* (but not as a model) of biological nitrogen fixation, wherein the $V^{2+}$ centers simulate the reduced active molybdenum site and the $Mg(OH)_2$ host lattice the protective function of the apoprotein.

## Experimental Section

**Reagents and Chemicals.** All reagents and chemicals used that were commercially available were either of *"analytical"* or *"reagent"* grade purity and were used without further purification. Vanadium(II)-salt stock solutions were prepared by reducing solutions of vanadyl sulfate in 1 N HCl with metallic zinc as outlined in ref 1 and standardized by titration with standard $Ce^{4+}$ solution. For the experiments in $D_2O$ the V(II) solutions were prepared analogously in pure $D_2O$ with careful avoidance of any contamination with protons or $H_2O$, as will be outlined below.

**Assays and Product Identification.** Hydrazine was determined spectrophotometrically by the method of Watt and Chrisp[16] as modified by us.[1] Hydrocarbons were measured by GLC, using a Varian Series 1200 Aerograph instrument equipped with a 6-ft Durapak phenyl isocyanate-Porasil, 80-100 mesh column. Identification of hydrocarbons was performed by measurements of retention times and coinjection of authentic compounds. In doubtful cases, mass spectrographic analysis was employed. $H_2$ was determined by GLC using a 6-ft column filled with molecular sieve (5 Å), at 27 °C.

**Experimental Technique for Studies with Substrates Other Than Nitrogen.** Aliquots of the V(II) stock solution, i.e., 0.10-0.15 mL, corresponding to about 40 $\mu$mol of $V^{2+}$, 2 mL of $CH_3OH$, and 2 mL of aqueous 1 M $MgSO_4$ solution were injected into rubber-capped glass bottles of 38-mL capacity. These were previously flushed with pure argon or the reducible gaseous substrates, depending on the nature of the experiment. At $t = 0$, 7 mL of 8 N KOH was injected rapidly and the bottles were shaken to assure rapid homogenization of the reaction mixture and uniform metal-hydroxide-gel formation. At various time points, gas samples were withdrawn and analyzed for hydrocarbon products or $H_2$ as described above. In the experiments with liquid substrates, these were as a rule injected in amounts of 570 $\mu$mol (a convenient amount for the scale of most experiments) prior to the addition of the 8 N KOH solution. Where gaseous substrates (e.g., alkyl halides) had to be added, 12.7 $cm^3$ of the respective gases at 1 atm was injected into the bottles by means of a syringe. To spot leaks the bottles were immersed into water-filled beakers and the gas injections were performed under water. This simple procedure facilitated the detection of any leakage.

**Nitrogen Reduction Experiments.** Typical experiments were performed as outlined above for gaseous substrates except that the glass bottles of 38-mL capacity were first filled with pure $N_2$ at 1 atm. After addition of the V(II) salt solution, $MgSO_4$, and $CH_3OH$, the hydroxide gels were generated by the injection of 7 mL of 8 N KOH at room temperature. After specified times the solutions were analyzed for $N_2H_4$ (and occasionally also for $NH_3$) by centrifuging the reaction suspension followed by careful acidification of the supernatant with 6 N HCl in the predetermined amount to bring the terminal pH to 1. The acidified solutions were diluted to a volume of 25 mL. Hydrazine was determined colorimetrically with *p*-dimethylaminobenzaldehyde reagent,[16] and ammonia (for control purposes), by the method of Kruse and Mellon.[17]

**Experiments in $D_2O$.** Deuterium oxide of 99.5% isotopic purity was purchased from Strohler Isotopes Inc. The V(II) salt solution was prepared by reducing solutions of anhydrous $VCl_3$ with dried mossy zinc in 1 $D_2O$. The DCl required for this purpose was generated by reacting $SOCl_2$ with $D_2O$. The $SO_2$ was removed by purging the resulting solutions with pure, dried argon, followed by brief evacuation. Solutions of NaOD, 8 N in $D_2O$, were prepared by dissolving the calculated amounts of metallic sodium in $D_2O$ under argon. They were standardized by titration with 1 N HCl and, where necessary, diluted to the same normality as the corresponding solution of NaOH in $H_2O$. Methanol-*O-d* was purchased from Aldrich at 99.5% purity. In order to assure comparable reaction conditions, all experiments in $D_2O$ were performed together with controls in $H_2O$ under the same conditions.

**Effects of Additives.** Studies of the effects of alcohol additives on the efficiency of $N_2$ reduction were performed under the standard reaction conditions described above, i.e., the alcohols were added to the reaction solutions prior to gel formation. Ethanolamine and the other amines tested were added *after* the gels had been formed or as indicated in the legends to Figures 3 and 4 or Table II.

**Miscellaneous Experiments.** The experiments with gaseous inhibitors are straightforward and were performed under the same conditions as those with the gaseous substrates. Inhibition of substrate reduction by $CN^-$ involved the injection of freshly prepared 2 M solutions of NaCN *after* the gels had been generated (this is essential as $CN^-$ forms complexes with V(II) which cannot be incorporated into the $Mg(OH)_2$ lattice). The reduction of $CN^-$ to $NH_3$ and $CH_2=O$ was demonstrated by determining $NH_3$ colorimetrically in distillates of reaction centrifugates; $CH_2=O$ was detected qualitatively in the undistilled supernatants with chromotropic acid-$H_2SO_4$.[18] Control assays in solutions of NaCN in the *absence* of V(II) were performed which were negative for $CH_2=O$; traces of $NH_3$ were detected in the distillates but at significantly lower concentrations than in the runs with V(II) present. Diazomethane was generated from Diazald according to Boer and Backer[19] except that the required KOH solution was replaced by 8 N NaOH. Using 0.2 g of Diazald and 10 mL of 8 N NaOH, to which 3 $cm^3$ of $CH_3OH$ and 3 $cm^3$ of diethyl ether were added, the resulting biphasic solution of diazomethane and NaOH could be used directly for the production of the $V(OH)_2$-$Mg(OH)_2$ gels in place of the 8 N NaOH solution employed in the other experiments. Dimethyldiazene, $CH_3N=NCH_3$, was prepared[20] from *s*-dimethylhydrazine by oxidation with freshly precipitated HgO; diazirine was synthesized as described in the literature;[21] the respective reduction experiments were performed by injecting methanolic solutions of the compound to $V(OH)_2$-$Mg(OH)_2$ suspensions (this substrate must not be added to acidic V(II) solutions as it is also reduced under these conditions). Diaziridine was identified by GLC and mass spectroscopy. *s*-Dimethylhydrazine was detected by UV spectroscopy after reoxidation to dimethyldiazene with HgO. In the reduction of diaziridine, formaldehyde was detected by means of chromotropic acid-$H_2SO_4$, and ammonia according to Kruse and Mellon,[17] in distillates of the reaction centrifugates.

**Determination of the Stereochemical Course of $C_2H_2$ Reduction in $D_2O$.** The reduction of $C_2H_2$ by $V(OD)_2$-$Mg(OD)_2$ was scaled up to obtain sufficiently high yields of product $C_2H_2D_2$. A $VCl_2$ solution in 1 mL of 4 N DCl, corresponding to 200 mol of $V^{2+}$ and 10 mL of a 1 M $MgSO_4$ solution in $D_2O$, was injected into a rubber serum-capped, $C_2H_2$-filled (1 atm) glass bottle of 160-mL capacity. The reduction was initiated by the injection of 5 mL of 1 M NaOD. (The lower base concentration was chosen to suppress the base-catalyzed exchange of acetylenic protons.) After 30 min of reaction, the gaseous contents of the reaction bottle were transferred into an evacuated IR gas cell. The region between 1000 and 800 $cm^{-1}$ was recorded and revealed a sharp band at 842.1 $cm^{-1}$, characteristic of $\omega_7$, a nonplanar vibrational mode of *cis*-1,2-$C_2H_2D_2$.[22] No band or shoulder was observed in the region of 987-990 $cm^{-1}$ where $\omega_4$, a characteristic frequency of *trans*-$C_2H_2D_2$, would have been expected.[22]

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(10) This is mainly because solvolysis reactions of the alkyl halides occur under the reaction conditions and differences in the solubilities of the compounds would have to be considered for quantitative comparisons.
(11) This property of Mg(OH)₂ can be strikingly demonstrated by exposing the iodine-inclusion complex of Mg(OH)₂ to alkali. Whereas I₂ undergoes base-induced disproportionation noticeably already at pH 8.5. the Mg(OH)₂–I₂ inclusion complex can be suspended in solutions of pH 10 without losing its dark brown color.
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# Molecules with $T$ Symmetry. Conformational Analysis of Systems of Type M[C(CH₃)₃]₄ and M[Si(CH₃)₃]₄ by the Empirical Force Field Method

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**Abstract:** Empirical force field calculations have shown that compounds of the type M[C(CH₃)₃]₄ and M[Si(CH₃)₃]₄, where M is an element of group 4A, exist in at least two conformational states: a ground state with $T$ symmetry, and a higher energy conformer with $S_4$ symmetry. In addition, a $C_2$ form has been found for C[C(CH₃)₃]₄ (**2**). The energy gap between the $T$ and $S_4$ forms increases with a decrease in the central M–C or M–Si bond length, and reaches a maximum of 16 kcal/mol for the most strained member of the series, **2**.

The symmetry of every molecule—properly speaking, of every molecular model—under the rigid body approximation may be described by some point group, and that of a chiral molecule by one of five: $C_n$, $D_n$, $T$, $O$, and $I$. Curiously, whereas molecules with $C_n$ or $D_n$ symmetry are commonplace,[1] chemical representatives of the remaining three groups are generally considered to be unknown.[2] This state of affairs is rendered the more remarkable by the fact that $T$, $O$, and $I$ are the pure rotation groups of the well-represented achiral tetrahedral ($T_d$ and $T_h$),[4] octahedral ($O_h$),[5] and icosahedral ($I_h$)[6] groups, respectively.

Chemical structures belonging to one of these chiral groups are readily envisaged: it is merely necessary to combine an achiral skeleton of the appropriate symmetry with a set of ligands which preserves all symmetry elements of the first kind while destroying all those of the second.[7] This principle underlies the elaborate design of various hypothetical molecules with $T$[1,8] and $O$[9] symmetry.[10] Over 30 years ago, Herzberg,[11] applying the same principle, pointed out that $T$ symmetry is exhibited by any conformation of neopentane, C(CH₃)₄, in which each methyl group is twisted in the same sense and to the same extent ($0 < \phi < \pi/3$) relative to a $T_d$ conformation ($\phi = 0$ or $\pi/3$).[12] The present paper is devoted to a fuller exploration of Herzberg's appealingly simple idea by an examination of conformational preferences in molecules of the type MR₄, where M is an element of group 4A and R = C(CH₃)₃ or Si(CH₃)₃.

**Symmetry and Time Scale.** Central to the definition of molecular symmetry is the time scale of measurement to which the symmetry refers. In discussing nonrigid molecules which can undergo internal torsional motion, such as neopentane and molecules of the type MR₄, it is therefore essential to specify the particular model of the molecule which is appropriate to

the conditions of measurement. The symmetry label attached to that model is then a fair expression of "molecular symmetry" under the stated conditions.[13]

For nonrigid molecules the appropriate group is the Longuet-Higgins molecular symmetry (MS) group,[14] which may be conveniently expressed as the semidirect product of the torsional subgroup of the ligands and the frame subgroup of the skeleton.[15] In the context of the present discussion, it is instructive to examine the case of a molecule of the type CR*₄, where R* is an asymmetric ligand and all four ligands have the same absolute configuration.[16] The highest point group symmetry possible for such a molecule is $D_2$,[1] and all conformations of CR*₄ must therefore belong to $D_2$ or to one of its subsymmetries (i.e., $C_2$ or $C_1$). However, we might be dealing with a nonrigid molecule, and the appropriate symmetry group in that case is the MS group, with feasible transformations corresponding to the internal motions of the molecule. The molecular symmetry group is therefore $(C_1)^4 \wedge T$, a group of order 12 which is isomorphic to $T$. In other words, the symmetry of time-averaged CR*₄ is *permutationally equivalent to $T$.*[17]

Similarly, seen as a rigid structure, neopentane has $T_d$ symmetry in the ground state.[18] On the other hand, viewed as a structure in which internal rotations of the methyl groups are time averaged, the molecular symmetry group of neopentane[15] is $(C_3)^4 \wedge T_d$, of order 1944. Evidently, Herzberg's $T$ symmetry for neopentane refers to a molecule frozen into a conformation which is unstable relative to the $T_d$ ground state.

**Static and Dynamic Symmetry of Tetrakis(trimethylsilyl)-silane (1).** In 1970 an electron diffraction study by Bartell et al.[19] showed that Si[Si(CH₃)₃]₄ (**1**), a silicon analogue of the unknown C[C(CH₃)₃]₄, exhibits $T$ symmetry in the gas phase. Bartell et al. suggested that the deformation from $T_d$ symmetry