Results of conductivity studies of this compound are consistent with its formulation as a 1:1 electrolyte.

Acknowledgment. We are grateful to the National Science Foundation (Grant No. CHE78-07913) for support of this research. The JEOL FX-90Q and IBM-IR98 instruments were purchased with funds provided partially by the NSF. We thank Dr. Ruth A. Pickering for exploratory work on this project.

Registry No. I, 80890-32-0; II, 80890-33-1; III, 80890-34-2; IV, 74237-51-7; V, 74237-52-8; VI, 80951-31-1; VII, 80890-35-3; VIII, 80890-36-4; IX, 74237-58-4; X, 74237-57-3; XI, 74237-55-1; XII, 80890-38-6; XIII, 74252-09-8; XIV, 74237-61-9; XV, 74237-60-8; DiNC, 74255-20-2; *t*-BuDiNC, 80878-98-4; DiCN, 74255-19-9; $DiNO_2$, 51661-19-9; *t*-$BuDiNO_2$, 80878-99-5; $DiNH_2$, 52411-34-4; *t*-$BuDiNH_2$, 75030-59-0; DiFor, 74255-22-4; *t*-BuDiFor, 80879-00-1; 2-nitrophenol, 88-75-5; 1,2-dichloroethane, 107-06-2; acetic formic anhydride, 2258-42-6; 4-*tert*-butylphenol, 88-18-6; 4-*tert*-butyl-2-nitrophenol, 3279-07-0; 2-cyanophenol, 611-20-1; $Cr(CO)_4(nor)$, 12146-36-0; $Mo(CO)_4(nor)$, 12146-37-1; *cis*-$Mo(CO)_4(pip)_2$, 65337-26-0; *cis*-$W(CO)_4(pip)_2$, 56083-13-7; $(Et_4N)[Cr(CO)_5I]$, 14780-98-4; $(Et_4N)[W(CO)_5I]$, 14781-01-2; $Mn(CO)_5Br$, 14516-54-2; $[CpFe(CO)_2(CS)]PF_6$, 34738-61-9; $[CpFe(CO)_3]PF_6$, 38834-26-3; $PtCl_2(PhCN)_2$, 15617-19-3.

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Hydrogen-Evolving Systems. 5. Nitrogen Reduction in the $V(OH)_2/Mg(OH)_2$ and $V(OH)_2/ZrO_2 \cdot H_2O$ Systems: Factors Influencing Selectivities and Yields of Hydrazine and Ammonia Production

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New observations are reported for the reduction of molecular nitrogen in the $V(OH)_2/Mg(OH)_2$ and $V(OH)_2/ZrO_2 \cdot H_2O$ systems. The reduction of N_2 can be directed to yield predominantly hydrazine or ammonia by selecting appropriate reaction conditions. Hydrazine is formed preferentially if the reduction of N_2 is conducted at high dilution, at high N_2 pressures, at low $V(OH)_2/Mg(OH)_2$ ratios, and at high NaOH concentrations. Under these conditions only traces of ammonia are formed because the secondary reduction of product hydrazine to ammonia is effectively suppressed. Trapping experiments and the observed yields of hydrazine on $p_{N_2}{}^2$ are consistent with the previously proposed mechanism of hydrazine formation through the disproportionation of diazene and rule out a direct reduction of N_2 to N_2H_4. The formation of ammonia is favored at small reaction solution volumes, at high $V(OH)_2/Mg(OH)_2$ ratios, and at low NaOH concentrations. In the $V(OH)_2/ZrO_2 \cdot H_2O$ system, the yields of ammonia and of hydrazine are generally lower but depend qualitatively on the same variables. The ammonia is formed by the secondary reduction of product hydrazine by $V(OH)_2$.

Introduction

In 1970, Shilov and co-workers observed that coprecipitated alkaline suspensions of $V(OH)_2$ and $Mg(OH)_2$ reduce molecular nitrogen to hydrazine and ammonia.[1] The Russian workers subsequently suggested that N_2H_4 is formed from N_2 directly by way of a "collective 4-electron-transfer process".[2-4] Assuming that $V(OH)_2$ acts as a 1-electron reductant, they postulated the reduction to take place in clusters of four or more V^{2+} ions at the $Mg(OH)_2$ surface. An analogous mechanism was also proposed for the reduction of C_2H_2 to C_2H_6 by $V(OH)_2/Mg(OH)_2$.[4]

In contrast, our work[5-7] has demonstrated that $V(OH)_2$ acts as a 2-electron reductant. The reduction of N_2 to N_2H_4 in the $V(OH)_2/Mg(OH)_2$ system was shown to occur in a stepwise fashion via diazene, N_2H_2, as the intermediate, and no evidence for the participation of V^{2+} clusters was obtained. We also demonstrated that the reduction of C_2H_2 in the $V(OH)_2/Mg(OH)_2$ system proceeds via C_2H_4 rather than directly to C_2H_6.

Maintaining their initial mechanistic ideas, Shilov et al. have since suggested[8] that NH_3 is formed directly from N_2 if the pH of the reaction medium is kept below 12. They also reject diazene as a possible intermediate of N_2 reduction on inappropriate thermodynamic grounds and on equivocal interpretations[9] of observed ^{15}N-isotope effects.

In the present paper, we will show that the stepwise mechanism of N_2 reduction[10] is also valid in the $V(OH)_2/Mg(OH)_2$ system under conditions leading to NH_3 and will present arguments against alternative mechanisms that have been proposed. In addition, we will also discuss the mechanistic significance of the kinetic ^{15}N-isotope effects described in ref 9. The experimental variables which determine the yields of NH_3 and N_2H_4 in reductions of N_2 by $V(OH)_2/Mg(OH)_2$ will be delineated first. Mechanistic aspects of N_2 reduction to NH_3 will be discussed next with particular reference to the intermediate formation of N_2H_2 and N_2H_4. Finally, new information on the reduction of N_2 in the $V(OH)_2/ZrO_2 \cdot H_2O$ system will be reported.

Results

Nitrogen Reduction in the $V(OH)_2/Mg(OH)_2$ System. The reduction of N_2 to either N_2H_4 or NH_3 depends on the relative concentrations of $V(OH)_2$ in the $Mg(OH)_2$ gels, on p_{N_2}, on reaction temperature, on the concentration of aqueous base,

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[1] N. T. Denisov, O. N. Efimov, N. I. Shuvalova, A. K. Shilova, and A. E. Shilov, *Zh. Fiz. Khim.*, **44**, 2694 (1970).

[2] A. E. Shilov, N. T. Denisov, O. N. Efimov, N. F. Shuvalov, N. I. Shuvalova, and E. Shilova, *Nature (London)*, **231**, 460 (1971).

[3] N. T. Denisov, N. I. Shuvalova, and A. E. Shilov, *Kinet. Katal.*, **14**, 1325 (1973).

[4] A. E. Shilov, *Usp. Khim.*, **43**, 378 (1974).

[5] S. I. Zones, M. R. Palmer, J. G. Palmer, and G. N. Schrauzer, *J. Am. Chem. Soc.*, **100**, 2133 (1978).

[6] S. I. Zones, T. M. Vickrey, J. G. Palmer, and G. N. Schrauzer, *J. Am. Chem. Soc.*, **98**, 7289 (1976).

[7] G. N. Schrauzer, N. Strampach, M. R. Palmer, and S. I. Zones, *Nouv. J. Chim.*, **5**, 5 (1981).

[8] N. T. Denisov, S. I. Kobelova, A. E. Shilov, and N. I. Shuvalova, *Kinet. Katal.*, **21**, 1257 (1980).

[9] L. A. Nikonova, S. Rummel, A. E. Shilov, and M. Wahren, *Nouv. J. Chim.*, **4**, 427 (1980).

[10] G. N. Schrauzer, *Angew. Chem.*, **87**, 579 (1975); *Angew. Chem., Int. Ed. Engl.*, **14**, 514 (1975).

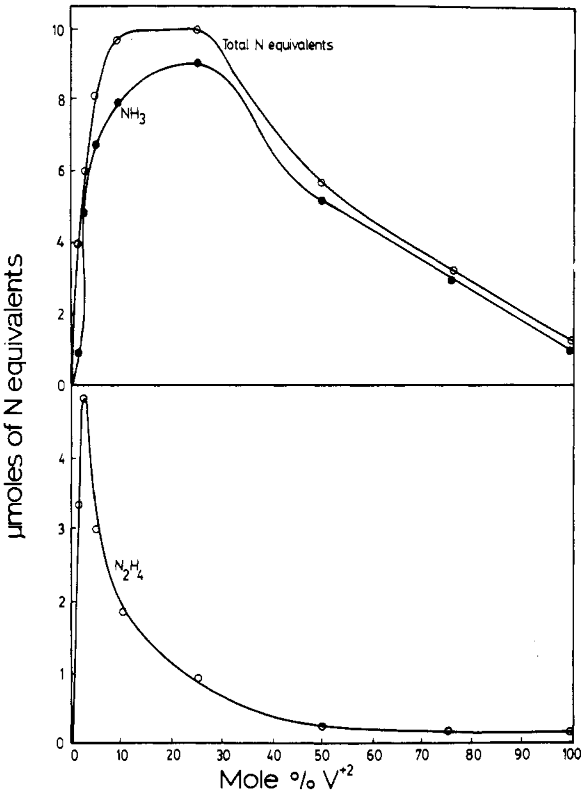

Figure 1. Reduction of N_2 (at 1.33 atm of pressure and 23 °C) over the complete composition range of the binary system $V(OH)_2/Mg(OH)_2$ in aqueous methanolic NaOH. The sum of the molar fractions of $V(OH)_2$ and $Mg(OH)_2$ was 2000 µmol, precipitated in a total reaction volume of 10 cm^3 of aqueous 5.6 M NaOH containing 20% (v/v) CH_3OH.

and on the total reaction solution volume. Because of their complexity, the effects of these variables will be described first. Figure 1 shows that the yields of N_2H_4 reach a maximum at low $V(OH)_2$ concentrations, while NH_3 becomes the main product at high $V(OH)_2$ concentrations. Although N_2 is still reduced in gels consisting predominantly of $V(OH)_2$, the yields of reduced-nitrogen products decline with decreasing $Mg(OH)_2$ concentration and become very low for pure $V(OH)_2$. The yield maximum for N_2H_4 shifts to higher $V(OH)_2/Mg(OH)_2$ ratios with increasing N_2 pressure. It may be expected that N_2 at higher pressures can compete more effectively with N_2H_4 for V^{2+} sites in the gel.

Effect of Temperature. Figure 2 shows the yields of N_2H_4 from experiments in the temperature range between 0 and 100 °C. Under the experimental conditions chosen, the yields of N_2H_4 increase up to the temperature of 85 °C. The subsequent decline at higher temperatures is mainly attributed to diminished solubility of N_2 in the liquid phase and the more rapid ageing of the gels at high temperatures. (Through direct tests with added N_2H_4, the declining yields at higher temperatures were shown not to be due to a decomposition of N_2H_4.)

Effects of Gel Aging. So that maximum yields of N_2H_4 and NH_3 could be achieved, the $V(OH)_2/Mg(OH)_2$ gels were invariably generated in the presence of N_2 substrate. In this manner, gel-aging effects can be minimized. If the gels are preformed, e.g., under argon, and N_2 or other reducible substrates are admitted at later times, a progressive loss of reducing activity is observed due to gel aging,[5] as has also been noted in ref 10. Gel aging is in part retarded by generating the gel in a solution containing ca. 20% (by weight) CH_3OH by the addition of NaOH.

Effects of NaOH Concentration. In our previous studies, the concentrations of NaOH in the aqueous/methanolic phase

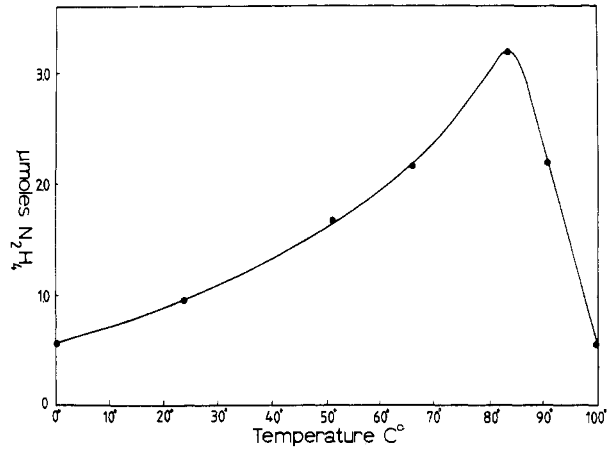

Figure 2. Temperature dependence of the yields of N_2H_4 from the reduction of N_2 with $V(OH)_2/Mg(OH)_2$. The gels contained 40 µmol of $V(OH)_2$ in 2000 µmol of $Mg(OH)_2$, suspended in 10 cm^3 of 5.6 M NaOH in H_2O containing 20% (v/v) CH_3OH. The yields of N_2H_4 were determined after 5 min of reaction at 1.3 atm of N_2 and the temperatures indicated. (Under these conditions only traces of NH_3 are formed and are not shown.)

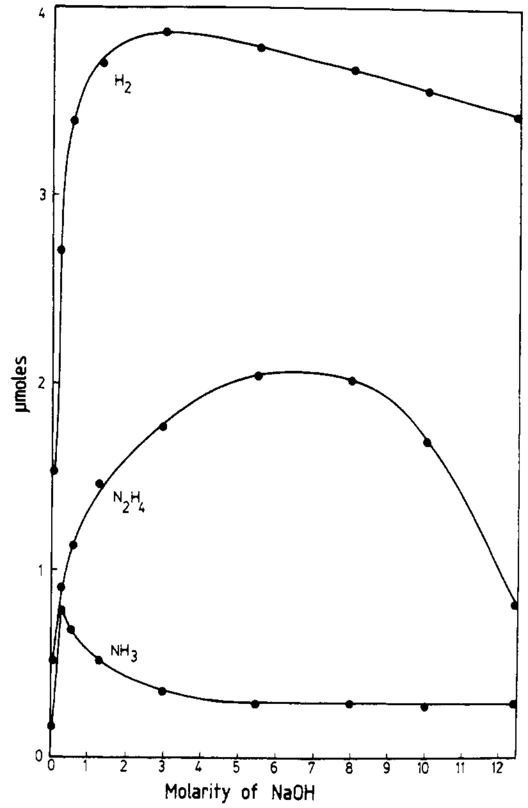

Figure 3. Effect of NaOH concentration on the yields of N_2H_4 and NH_3 at 25 °C. Other reaction conditions are the same as given in legend to Figure 2.

was chosen to be about 6 M. The high concentrations of NaOH were selected primarily to suppress the concomitant, substrate-independent hydrogen evolution. Although H_2 is produced from $V(OH)_2$ more rapidly at lower NaOH concentrations, we have observed significant yields of NH_3 and N_2H_4 at NaOH concentrations even below 0.01 M (Figure 3). At NaOH concentrations above 8 M, the yields of N_2H_4 and of NH_3 decline in a manner paralleling the diminishing solubility of N_2 in the NaOH solutions, although viscosity and other effects may also contribute. The secondary reduction of N_2H_4 to NH_3 is favored at lower NaOH concentrations, giving rise to a yield maximum at 0.3 M NaOH. However, this maximum depends on the reaction conditions chosen, most

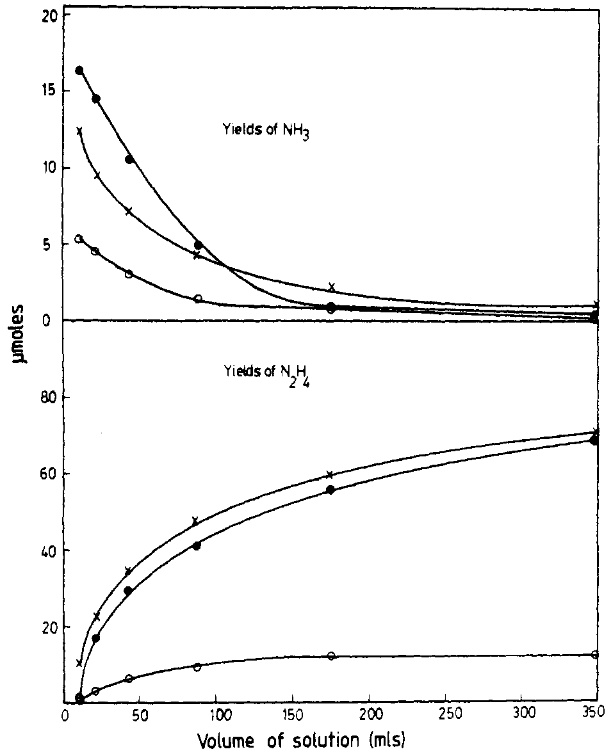

Figure 4. Yields of N_2H_4 and of NH_3 as a function of the total solution volume in N_2 reduction experiments at three different N_2 pressures (○, 0.5; ●, 1.3; ×, 2.6 atm). The gels contained 300 µmol of V(OH)$_2$/2000 µmol of Mg(OH)$_2$, precipitated in 5.6 M NaOH in 20% CH_3OH (v/v).

of all on the total reaction solution volume, as will be discussed below.

Effect of Reaction Solution Volume. Since most of the newly formed N_2H_4 first diffuses out of the $V(OH)_2/Mg(OH)_2$ gel before it is reduced to NH_3, the product N_2H_4 increasingly competes with N_2 for $V(OH)_2$ in the course of the reaction. When the reactions are conducted in large solution volumes, the secondary reduction of N_2H_4 can be effectively suppressed, as may be seen in Figures 4 and 5. Figure 4 shows that in 5.6 N NaOH higher yields of N_2H_4 are observed at all N_2 pressures investigated. The yields of NH_3, on the other hand, declined with increasing reaction solution volume and ultimately became negligible. In Figure 5, the dilution effect is demonstrated at pH 11.5. It may be seen that hydrazine is a major product at high solution volumes even at the much lower NaOH concentrations, indicating that NH_3 is still formed exclusively by the secondary reduction of product N_2H_4.

At sufficiently large reaction solution volumes, the overall yields of N_2H_4 approach 50% based on the stoichiometry of eq 1.

$$2V(OH)_2 + N_2 + 2H_2O \rightarrow N_2H_4 + 2O{=}V(OH)_2 \qquad (1)$$

Even at higher N_2 pressures, the yields are limited to 50% due to the comparatively low solubility of N_2 and the V(II)-consuming side reaction eq 2.

$$H_2O + V(OH)_2 + O{=}V(OH)_2 \rightarrow 2V(OH)_3 \qquad (2)$$

Thus, the overall reaction follows the apparent stoichiometry of eq 3.

$$4V(OH)_2 + N_2 + 4H_2O \rightarrow N_2H_4 + 4V(OH)_3 \qquad (3)$$

Detection of Diazene. In an extension of previous experiments,[5,6] actively N_2-reducing reaction suspensions were stopped at various time points both with and without added allyl alcohol and under conditions which yield predominantly NH_3 rather than N_2H_4. Allyl alcohol is an effective "diazene scavenger" because it reacts with N_2H_2 according to eq 4.[11]

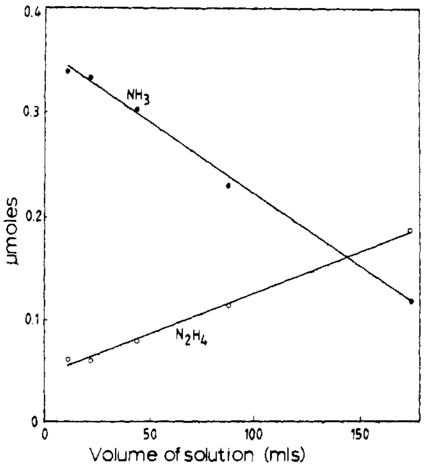

Figure 5. Yields of N_2H_4 and of NH_3 as a function of the total solution volume in N_2 reduction experiments at 1.3 atm. The gels contained 70 µmol of V(OH)$_2$/2000 µmol of Mg(OH)$_2$, precipitated in NaOH of solutions in 20% CH_3OH. The solution pH was 11.5 in all cases.

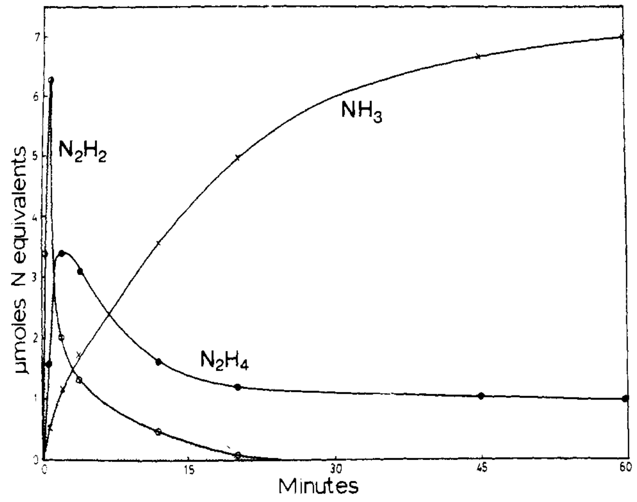

Figure 6. Appearance and disappearance of intermediates in the reduction of N_2 to NH_3 at 1.3 atm. The gels contained, in a total volume of 10 cm^3, 70 µmol of V(OH)$_2$/2000 µmol of Mg(OH)$_2$ in 5.6 M NaOH and 20% CH_3OH (v/v). The concentrations of N_2H_2 at different time points were determined from the difference of the N_2H_4 yields observed on quenching with and without allyl alcohol. For quenching, 500 µmol of allyl alcohol was added at the specified reaction times. In the control tubes, propanol was added in place of allyl alcohol.

$$N_2H_2 + CH_2{=}CHCH_2OH \rightarrow N_2 + CH_3CH_2CH_2OH \qquad (4)$$

Hence, by determining the yields of N_2H_4 in separate experiments conducted in the presence and absence of allyl alcohol, the stationary concentrations of N_2H_2 can be calculated. Figure 6 shows that the concentrations of N_2H_2 reach a maximum during the first 2 min of reaction. They decline subsequently in a manner consistent with a second-order reaction while N_2H_4 is formed.

Effect of N_2 Pressure. Under conditions where N_2H_4 is the principal product of N_2 reduction, i.e., at high solution volumes and low $V(OH)_2$ concentrations, the yields of N_2H_4 approach 100% of the stoichiometry of eq 3 at N_2 pressures above 1.3 atm (see Figure 4). In the pressure range between 0.1 and 1.3 atm, the yields of N_2H_4 depend linearly on $p_{N_2}{}^2$ (see Table

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[11] E. E. van Tamelen, R. S. Dewey, and R. J. Timmons, *J. Am. Chem. Soc.*, **83**, 3725 (1961).

Table I. Yields of N_2H_4 as a Function of N_2 Pressure[a]

p_{N_2}, atm	yield of N_2H_4, μmol	% yield (eq 3)[b]	p_{N_2}, atm	yield of N_2H_4, μmol	% yield (eq 3)[b]
0.1	0.40	0.5	2.6	69.0	92
0.5	9.80	13	10	71.3	95
1.0	40.50	54	34	72.8	97
1.3	67.0	89			

[a] Reaction suspensions contained 300 μmol of $V(OH)_2$ and 2000 μmol of $Mg(OH)_2$. The total reaction solution volume was 350 cm³ of 5.6 M NaOH in 20% CH_3OH. All experiments were performed at 23 °C; N_2H_4 yields were determined after 5 min of reaction. [b] Given in terms of eq 3.

Table II. Yields of NH_3 at Different N_2 Pressures

p_{N_2}, atm	yield, μmol		p_{N_2}, atm	yield, μmol	
	NH_3	N_2H_4		NH_3	N_2H_4
0.1	0.81	0.11	1.3	16.3	0.22
0.5	5.1	0.15	2.6	12.5	11.5

[a] Reaction conditions are as given in legend of Table I except that the total reaction solution volume was 11 cm³ of 5.6 M NaOH in 20% CH_3OH.

I). At higher N_2 pressures, the yields no longer increase appreciably as they are essentially quantitative in terms of the stoichiometry of eq 3.

Under conditions where NH_3 is formed as the main product, i.e., when small reaction solution volumes and high $V(OH)_2$ concentrations are employed, the yields of NH_3 depend on the pressure of N_2 in a nonmonotonic fashion, declining at high N_2 pressures in favor of an increased formation of N_2H_4, as N_2 competes with N_2H_4 for $V(OH)_2$ reducing sites (see Table II).

Nitrogen Reduction in the $V(OH)_2/ZrO_2{\cdot}H_2O$ System. The dependence of the yields of N_2H_4, NH_3, and H_2 on the concentration of $V(OH)_2$ in the $ZrO_2{\cdot}H_2O$ gels is shown in Figure 7. At all $V(OH)_2{:}ZrO_2{\cdot}H_2O$ ratios, N_2 reduction is less efficient than in the $V(OH)_2/Mg(OH)_2$ system, while H_2 production is significantly enhanced. Moreover, the formation of NH_3 is favored over that of N_2H_4. As in the $V(OH)_2/Mg(OH)_2$ system, the yields of N_2H_4 can be increased by conducting the reaction at high solution volumes. Figure 8 shows, however, that the yields of NH_3 decline at higher solution volumes.

Discussion

Stepwise Reduction of Nitrogen to Hydrazine. The present paper provides new experimental data that are consistent with the previously proposed stepwise mechanism of reduction of N_2 to N_2H_4.[5,6] Diazene, N_2H_2, the first product of N_2 reduction, is formed within the protective $Mg(OH)_2$ or $ZrO_2{\cdot}H_2O$ lattice.[5,6] It is itself not reduced but disproportionates into N_2 and N_2H_4. The N_2H_4 thus generated diffuses out of the protecting gels into the reaction solution; in its subsequent reduction to NH_3 it has to compete with N_2 for $V(OH)_2$ reduction sites. By increasing the reaction solution volume at low $V(OH)_2{:}Mg(OH)_2$ ratios, the secondary reduction of product N_2H_4 can be effectively suppressed. Under optimal conditions, yields of N_2H_4 are virtually quantitative in terms of eq 3 and only traces of NH_3 are formed.

Reduction of Nitrogen to Ammonia. The formation of NH_3, on the other hand, is favored in small solution volumes and at high $V(OH)_2$ concentrations in the $Mg(OH)_2$ gels. This observation allows the interpretation of the results of the authors of ref 8, who performed most of their experiments in small solution volumes. They accordingly obtained high relative yields of NH_3 and little or no N_2H_4, especially below the pH of 12. This led them to the conclusion that NH_3 is formed directly from N_2 under these conditions. However, Figure 5 reveals that the yields of NH_3 are dependent on the total reaction solution volume. Moreover, the yields of NH_3 drop twice as steeply than the increase of N_2H_4, indicating that all NH_3 arises from the secondary reduction of N_2H_4 and none from a hypothetical direct 6-electron reduction of N_2.

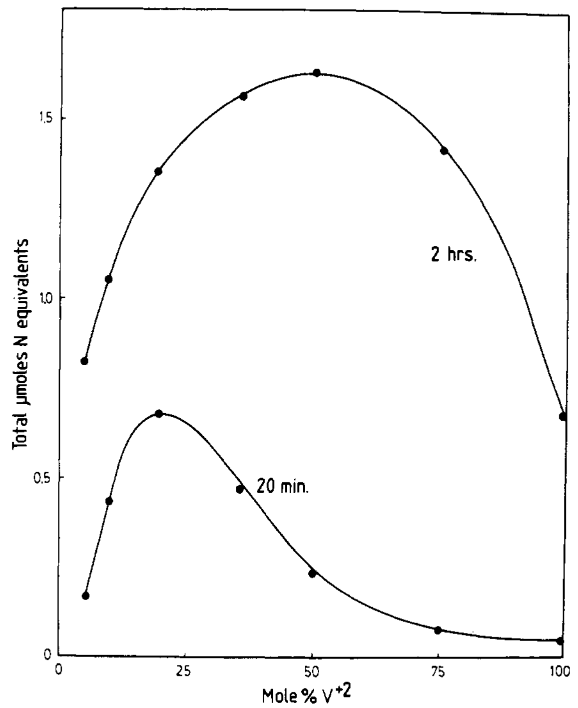

Figure 7. Reduction of N_2 at 1.3 atm of pressure in the $V(OH)_2/ZrO_2{\cdot}H_2O$ system. The gels contained a total of 400 μmol of $V(OH)_2$ and $ZrO_2{\cdot}H_2O$ in 10 cm³ of 5.6 M NaOH in 20% CH_3OH (v/v). Yield curves are shown after 20 min and 2 h of reaction.

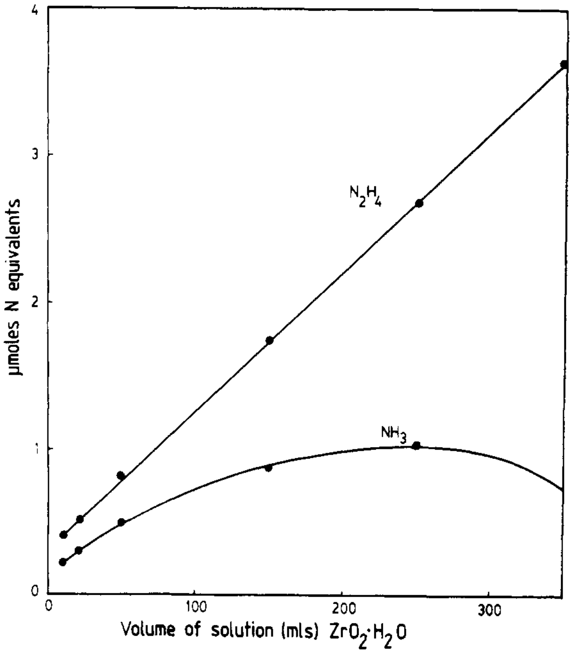

Figure 8. Yields of N_2H_4 and NH_3 as a function of total reaction solution volume on N_2 reduction (at 1.3 atm of pressure) in the $V(OH)_2/ZrO_2{\cdot}H_2O$ system. The gels contained 60 μmol of $V(OH)_2$/400 μmol of ZrO_2H_2O. Yields were determined after 1 h of reaction at 25 °C.

Intermediacy of Diazene. A linear dependence of the yields of N_2H_4 on $p_{N_2}{}^2$ is observed under conditions of N_2 reduction where N_2H_4 is the main product.[5] The data in Table I show the same result for N_2 reduction in the N_2 pressure range from

0.1 to 1 atm under the experimental conditions employed in the present paper. These results are consistent with the diazene disproportionation mechanism[5,6] and rule out any alternative mechanism invoking the direct reduction of N_2 to N_2H_4.

The intermediacy of N_2H_2 in the reduction of N_2 *under conditions where ammonia is the main product* was established through trapping experiments with allyl alcohol in analogy to previous experiments.[5,6] Figure 6 shows that a reactive intermediate accumulates during the early phases of reaction as expected. It disappears in a manner consistent with the known second-order disproportionation of diazene.

Nitrogen-15 Isotope Effects of Diazene Disproportionation. Nikonova et al.[9] recently attempted a measurement of kinetic ^{15}N-isotope effects of the reduction of N_2 in the $V(OH)_2/Mg(OH)_2$ system. Since earlier theoretical considerations of Rummel[12] suggested that the diazene disproportionation, eq 5, should be accompanied by a measurable kinetic isotope

$$2N_2H_2 \rightarrow N_2 + N_2H_4 \qquad (5)$$

effect, the authors hoped to obtained evidence for or against the diazene disproportionation mechanism. Wahren et al.[13] previously considered the observed enrichment of ^{15}N in the product hydrazine as positive evidence for the intermediacy of diazene.

However, they were unable to measure this effect in the more recent work.[9] Instead, they observed the ^{15}N kinetic isotope effect of the secondary reduction of N_2H_4 to NH_3 (eq 6). The authors of ref 9 performed all experiments after

$$N_2H_4 + V^{2+} \rightarrow [VNH_2NH_2]^{2+} \xrightarrow[O{=}V^{4+}]{+H_2O} 2NH_3 \qquad (6)$$

comparatively long reaction times (1–24 h), i.e., under conditions where the reduction of N_2H_4 to NH_3 was the main ongoing reaction. So the kinetic isotope effect of N_2H_2 disproportionation could be observed, the measurements should have been performed after short reaction times, e.g., after 1–10 min, when N_2H_4 is rapidly formed and its reduction to NH_3 occurs only to a minor extent. Isotope enrichment studies by themselves cannot be used to prove or disprove the intermediacy of compounds in the situation where the reaction pathway involving the labeled atom is multistep and includes most importantly several irreversible reaction steps and several equilibria.

Reduction of N_2 in the $V(OH)_2/ZrO_2{\cdot}H_2O$ System. The reduction of N_2 in the $V(OH)_2/ZrO_2{\cdot}H_2O$ system[5,6] proceeds by the same general stepwise mechanism albeit with lower efficiency. This is ascribed to the greater tendency of $ZrO_2{\cdot}H_2O$ to stimulate H_2 production from $V(OH)_2$. We consider this to be mainly due to the higher "intrinsic acidity" of $ZrO_2{\cdot}H_2O$ gels as compared to $Mg(OH)_2$. Indeed, with appropriate organic dyes as indicators (alizarin and Clayton Yellow), the "intrinsic pH" of $ZrO_2{\cdot}H_2O$ suspended in 1 M NaOH was found to be 10.5, while that of $Mg(OH)_2$ under the same conditions is 11.5. This difference in intrinsic acidity may be sufficient to account for the observed reactivity differences. However, structural factors and differences in the rates of ageing between $Mg(OH)_2$ and $ZrO_2{\cdot}H_2O$ gels may also be important as both determine the degree of interaction of the substrates with the $V(OH)_2$ reducing sites.

Summary. In summary, the present work proves that the reduction of N_2 to NH_3 by $V(OH)_2/Mg(OH)_2$ and $V(OH)_2/ZrO_2{\cdot}H_2O$ proceeds in a stepwise fashion via N_2H_4 and provides further strong support for the intermediacy of diazene in the reduction of N_2 to N_2H_4 in these systems.

Experimental Section

Reagents and Chemicals. All reagents and chemicals used were of analytical or reagent grade purity and were used without further purification. Vanadium(II) stock solutions, 1 M, in 2 M H_2SO_4, were prepared electrochemically from the method described by Brauer[14] except that Ar was used as the inert atmosphere instead of N_2.

Assays and Product Identification. Hydrazine was determined spectrophotometrically with the method of Watt and Chrisp[15] as modified by us.[6] Ammonia was assayed according to the method of Kruse and Mellon.[16] Hydrogen was determined quantitatively by gas chromatography using a column of 6-ft. length filled with 5-Å molecular sieves at 21 °C; a thermal conductivity detector was used with Ar as the carrier gas.

Standard Nitrogen Reduction Technique. The majority of experiments were run in glass bottles of 38 cm^3 capacity. These were first serum capped and subsequently flushed with N_2 gas (99.999%) for 15 min. The bottles were then injected with CH_3OH (2 cm^3), $MgSO_4$ solution (1 M, aqueous), 2 cm^3, and 1 aliquot of VSO_4 stock solution corresponding to 40 μmol of V^{2+}. At $t = 0$, 7 cm^3 of 8 M NaOH solution was injected into each bottle. During the addition of the NaOH, the bottles were shaken consistently for 15 s to ensure complete mixing and strictly comparable conditions. So that possible gas leakage could be prevented, the bottles should be held upside down. The experiments at N_2 pressures of up to 4 atm were performed in the same bottles. (Gas leaks were checked for by immersing the bottles into water.) For hydrogen determinations, gas samples were taken after the bottles were shaken for 15 s prior to sample withdrawal. For N_2H_4 and NH_3 analyses, the bottles were opened and the reaction suspensions centrifuged. The supernatants were transferred into volumetric flasks of 100-cm^3 capacity. After acidification to pH 1 with 2 M HCl, aliquots of the solutions were analyzed for NH_3 and N_2H_4 by the methods in ref 6 and 7. Modifications of this procedure are indicated in the legends of the figures.

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Registry No. N_2, 7727-37-9; $Mg(OH)_2$, 1309-42-8; $V(OH)_2$, 39096-97-4; $ZrO_2{\cdot}H_2O$, 12164-98-6; N_2H_4, 302-01-2; NH_3, 7664-41-7.

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