resonance and the exchanging resonance as a function of delay time to the magnetization equation was performed on a Commodore Pet computer. $\partial(M_A - M_B)/\partial t = (M_A - M_B)/T_1 - 2k_{ex}(M_A - M_B)$, M_A and M_B are the inverted resonance and the exchanging peak magnitudes, respectively. T_1 is the average relaxation time of these two protons; k_{ex} equals the exchange rate.

Kinetic Measurements of Alkyl Migrations. The rates of alkyl migrations were followed by FT NMR. Less than 45° observation pulses were used. Repetition rates were at intervals greater than twice the relaxation times of the protons being measured. Reaction temperatures were maintained by the probe temperature controller and observed to be constant to within 1° by measuring the peak separations of ethylene glycol. A typical reaction involved 30 mg of $Cp_2(PhCH_2)Nb{=}CHOZr(H)Cp^*_2$ (42 μmol) and 30 mg of diphenylacetylene (170 μmol) dissolved in 0.45 mL of benzene-d_6. As the reaction proceeded, the Cp resonance of starting material lost intensity as the Cp resonance due to $Cp_2Nb(H)(PhC{\equiv}CPh)$ appeared. The plot of the decay of the integrated intensity of the Cp proton resonance of starting complex as a function of time showed first-order behavior for more than 3 half lives. The rate for benzyl migration was independent of $PhC{\equiv}CPh$ concentration over a 50-fold range. Most migration rates were studied with only a three-fold excess of $PhC{\equiv}CPh$ yet displayed first-order kinetics for at least 3 half-lives.

Benzyl Migration Crossover Experiment. A 25-mg sample each of $Cp_2(PhCD_2)Nb{=}CHOZr(H)Cp^*_2$ and $Cp_2(PhCH_2)Nb{=}CDOZr(D)(Cp^*\text{-}d_{15})_2$ were mixed with 30 mg of diphenylacetylene in benzene-d_6. The reaction was monitored by NMR. The olefinic proton at δ 5.73 appears as a singlet for $Cp^*_2Zr(H)(OCH{=}CDPh)$; no doublet which would indicate $Cp^*_2Zr(H)(OCH{=}CHPh)$ was observed.

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Hydrogen-Evolving Systems. 4. The Reduction of Molecular Nitrogen and of Other Substrates in the Vanadium(II)–Pyrocatechol System

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Abstract: Reactions of molecular nitrogen and of other substrates with vanadium(II)–pyrocatechol complexes occur in two-electron steps at monomeric V(II) centers rather than by collective electron-transfer processes involving polynuclear clusters of vanadium(II)–pyrocatechol complexes. The reduction of acetylene, for example, obeys the stoichiometric equation $V^{II}PC + C_2H_2 + 2H^+ \rightarrow V^{IV}PC + C_2H_4$ at high substrate concentrations. At low concentrations of substrate acetylene or with less reactive substrates S, the overall reaction stoichiometries are expressed more closely by the equation $2V^{II}PC + S + 2H^+ \rightarrow 2V^{III}PC + H_2S$, primarily because of the concurrent side reaction $V^{II}PC + V^{IV}PC \rightarrow 2V^{III}PC$. In the absence of added reducible substrates, H_2 is evolved spontaneously according to the equation $2V^{II}PC + 2H^+ \rightarrow 2V^{III}PC + H_2$. The reduction of N_2 to NH_3 occurs in a stepwise fashion with N_2H_2 and N_2H_4 as the intermediates. The high reduction potential of N_2 to N_2H_2 and the tendency of N_2H_2 to decompose into the elements are mainly responsible for the extreme dependence of the yields of NH_3 on pH and solvent.

In recent papers of this series[1,2] we reported on the reduction of nitrogen and of other substrates in heterogeneous systems containing vanadium(II) hydroxide in inert host matrices such as $Mg(OH)_2$ or ZrO_2(aq). The reduction of N_2 with $V(OH)_2/Mg(OH)_2$ was originally shown by Shilov and his coworkers to yield hydrazine and ammonia,[3] and it was postulated that N_2 is reduced directly in clusters of two or four V(II) ions situated in the $Mg(OH)_2$ lattice.[4] However, other workers pointed out that such a reaction would be thermodynamically improbable.[5]

Our work established[1,2] that vanadium(II)-hydroxide acts as a 2-electron reductant and that the reduction of nitrogen to hydrazine takes place in a stepwise manner with the intermediate formation of diimide, N_2H_2, which disproportionates inside the host lattice into hydrazine and nitrogen.

Nikonova et al[6] reported in 1972 that complexes of V(II) with pyrocatechol (PC, 1,2-dihydroxybenzene) reduce molecular nitrogen to ammonia. The reaction was proposed[7-10] to proceed via a "collective four-electron-transfer mechanism" involving aggregates of two or four $V^{II}PC$ complexes which bind N_2 and reduce it directly to hydrazine. However, the existence of higher order $V^{II}PC$ complexes has not been adequately demonstrated, and no evidence for the collective four-electron-transfer mechanism of N_2 reduction has thus far been obtained.

We became interested in the reactions of N_2 with $V^{II}PC$ complexes because N_2 reduction is accompanied by a simultaneous production of hydrogen. At high N_2 pressures, the reaction stoichiometry has been given in terms of reaction 1.[7] Equation

$$N_2 + 8e^- + 8H^+ \rightarrow 2NH_3 + H_2 \qquad (1)$$

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1 suggested to us that N_2 is reduced in a stepwise fashion via diimide, in a manner similar to the reduction of N_2 in the $V(OH)_2/Mg(OH)_2$ system.[1,2]

To establish the reaction stoichiometry and other mechanistic details of reductions in the $V^{II}PC$ system, we also investigated reactions with reducible substrates other than nitrogen. This was necessary because it was previously assumed that $V^{II}PC$ clusters exist which act as two-, four-, six- or even eight-electron reductants. No such clusters or complexes have been isolated. Although $V^{II}PC$ complexes can be prepared in solution, they are metastable and decompose spontaneously with H_2 evolution even at low temperatures. Accordingly, we performed our experiments with $V^{II}PC$ complexes generated in situ, employing reaction conditions comparable to those used by the Russian workers. For most experiments, methanol was chosen as the solvent because ammonia is formed in detectable yields even at subatmospheric pressures of N_2.[6-10] In aqueous solutions N_2 is reduced as well, but high yields of NH_3 are observed only at high N_2 pressures[6-10] (e.g., 100 atm), for reasons to be discussed. Since diimide (diazene, N_2H_2) could be expected to be formed as an intermediate in the reduction of N_2 by $V^{II}PC$, we decided to study the reactions of authentic N_2H_2 generated in situ from tosyl hydrazide under the conditions of N_2 reduction in the $V^{II}PC$ system. The results of these experiments will also be reported.

Experimental Section

Reagents, Chemicals, and Stock Solutions. All chemicals and reagents were of either "analytical" or "reagent" grade commercial purity. Unless otherwise noted, all reagents were prepared and all experiments were performed with exclusion of oxygen obtained by purging with argon or nitrogen.

Pyrocatechol (99+%), from Aldrich, was vacuum sublimed at 50 μm of pressure and 100 °C. Of the colorless, crystalline sublimate, 1 M solutions in CH_3OH or H_2O were prepared. Such solutions can be stored in sealed bottles under argon and remain colorless for several weeks. A slight darkening of the solutions due to traces of oxygen may eventually occur but has no effect on performance in the experiments to be described below.

Stock solutions of V(II) in water or methanol were obtained by the dissolution of solid $VSO_4{\cdot}6H_2O$ obtained electrolytically from $VOSO_4{\cdot}5H_2O$.[11] The resulting solutions were standardized by titration with 0.1 N Fe(III), using safranine as the indicator.[12]

Carbonate-free stock solutions of $NaOCH_3$ were prepared by dissolving the calculated amount of reagent grade $NaOCH_3$ in CH_3OH. The solutions were standardized by acidimetry with Neutral Red as the indicator and stored in an atmosphere of argon. All stock solutions were diluted prior to use, as required.

Nitrogen gas (99.999%) was used without further purification. Acetylene was passed through a wash bottle filled with concentrated H_2SO_4. Ethylene was used as received. All three gases were obtained from Matheson. 2-Butyne, purchased from ICN Pharmaceuticals, and butadiene (1,3), from Matheson, were also used as received. Sodium azide (Alfa Inorganics) was of analytical grade purity; nitrous oxide was U.S.P. quality and obtained from Liquid Carbonic Corp. Carbon monoxide (99.9%, Matheson) was passed through a water-filled wash bottle prior to use. Tosyl hydrazide was reagent grade from Aldrich.

Assays and Product Identification. Ammonia was determined by the colorimetric method of Kruse and Mellon[13] in the steam distillates of the reaction solutions. Hydrocarbons were measured by GLPC at 27 °C, employing a 6-ft column filled with 80–100 mesh phenyl isocyanate–Poracil C, helium as the carrier gas, and a flame ionization detector. Hydrogen and nitrogen were measured by GLPC at 27 °C, utilizing a 6-ft molecular sieve 5A column, argon as carrier, and a thermal conductivity detector. H_2O was determined by Karl Fischer titration in the vacuum distillate of the reaction solution. In this case only, V(II) was obtained from the reduction of anhydrous VCl_3 by Zn in CH_3OH acidified with HCl gas. Ethanol (from acetaldehyde) and methanol (from CO and $CH_2{=}O$) were detected by mass spectroscopy in the distillate of reaction solutions with H_2O as the solvent. Hydrazine was determined by the method of Watt and Crisp.[14] Small aliquots of the reaction solutions were analyzed directly. Minor interferences from the other components in the solutions were compensated for by appropriate standardizations.

Table I. Acetylene Reduction by $V^{II}PC$: Dependence of the Yields of C_2H_4 and H_2 on C_2H_2 Concentration[c]

μmol of C_2H_2 added	μmol of C_2H_2 in soln	% yield	
		C_2H_4	H_2[a]
10	5.8	12[b]	38
40	23	31	19
80	46	46	4
200	120	69	3
600	350	82	2.5
3100 (=1 atm)	1800	86	2.3
4700	2700	95	tr
6200 (=2 atm)	3600	95	nd

[a] tr = trace; nd = not detectable. [b] Substoichiometric amount of C_2H_2 in solution; maximum possible yield, 25%. [c] Reaction solutions contained in a total volume of 5 mL: V(II), 40 μmol: PC and $NaOCH_3$, 2500 μmol each. In CH_3OH at 27 °C. Yields measured at t_∞ (= 1 h).

Standard Experimental Techniques. In typical experiments, 2.5 mL of a 1 M methanolic solution of pyrocatechol and 2.5 mL of a 1 M solution of sodium methoxide in methanol were injected into argon-filled, rubber serum capped glass bottles of 38-mL capacity. The substrate was then added, depending on which substrates were used, measured volumes of gases, liquids, or solutions of solid substances were injected directly into the reaction bottles. For experiments at high concentrations of gaseous substates, the bottles were initially flushed with the respective gas instead of argon. Above 1 atm of pressure, a known additional volume of the gaseous substrate was injected by means of a syringe. To initiate the reductions, e.g., we injected 0.10 mL of 0.40 M V(II) stock solution as the bottles were shaken vigorously and as rapidly as possible; this usually required no more than 0.1 s. The $V^{II}PC$ solutions obtained in this manner remain homogeneous throughout the experiment. At higher V^{II}–PC ratios of about 1:10, the solutions are homogeneous at first but become heterogeneous as the reaction proceeds. No difference in behavior or reactivity was observed when the $NaOCH_3$– instead of the V(II) solution was injected last.

Hydrocarbon products and hydrogen were determined by the periodic withdrawal of small gas samples (0.2 mL). Absolute yields were calculated from observed GLPC peak areas by comparison with standardization curves for the respective gases. The calibration curves were obtained from measurements under simulated experimental conditions [except for the presence of V(II), which was substituted by V(III) (as the chloride)], to avoid reduction reactions occurring during GLPC calibration measurements.

pH Measurements. The effective solution pH in CH_3OH was determined by anaerobic titration of pyrocatechol with $NaOCH_3$ solution using Alizarin Yellow R, thymolphthalein, and 5,5′-indigodisulfonic acid disodium salt as the indicators.

Kinetic Measurements. The rates of reduction of only a few substrates, e.g., of N_2, H^+, and C_2H_4, are sufficiently slow to be determined directly through yield measurements as a function of time. The rates of reduction of the remaining substrates in Table I were too fast to be measured directly. They were determined relative to each other and to the aforementioned directly measured rates by pairwise competition experiments. The ratio of the rates of two competing pseudo-first-order reactions is equal to the yield ratios of the products C and D, if A and B have equal *excess* initial concentrations.[15] If the rate constants of the two reactions are k_1 and k_2 and $[A]_0 = [B]_0$, then $[C]/[D] = k_1/k_2$, where k_1 and k_2 are defined by $A + [V(II)] \xrightarrow{k_1} C$ and $B + [V(II)] \xrightarrow{k_2} D$, respectively. In all experiments, the concentrations of pyrocatechol and of $NaOCH_3$ were 0.5 M. The concentrations of substrates were varied depending on their reactivity; the rates shown in Table I are expressed for equal concentrations of substrate, i.e., 0.1 M.

For the more reactive substrates, H_2 evolution was a negligible concurrent side reaction and was ignored in the analysis of relative rates greater than 10. The autocatalysis of H_2 evolution by V(III) produced only a small effect on the rates at very low V(II) concentrations and short times and therefore was neglected.

Solubilities of Gaseous Substrates. The solubilities of gaseous substrates were determined manometrically. Solubilities were measured in solutions identical with reaction solutions except for the replacement of V(II) by V(III).

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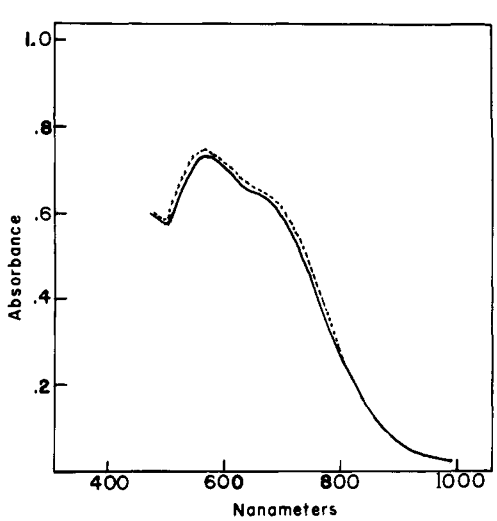

Figure 1. Optical absorption spectrum of methanolic reaction solution of $V^{II}PC$ following 2-atm C_2H_2 reduction. Dotted spectrum is of $V^{IV}PC$ prepared from $VOSO_4$. Both solutions were 0.5 M in $NaOCH_3$ and catechol and 1.0 mM in vanadium.

Table II. Ethylene Reduction by $V^{II}PC$: Dependence of the t_∞ Yields of C_2H_6 on C_2H_4 Concentration[b]

μmol of C_2H_4 added	μmol of C_2H_4 in soln	% yield	
		C_2H_6	H_2[a]
40	11	10	40
200	56	30	20
900	250	53	9
1800 (1 atm)	500	59	6
3600	1000	66	ND

[a] nd = not detected. [b] Reaction conditions as given in Table I.

Results

Reduction of Substrates Other than Nitrogen. Reactions of $V^{II}PC$ complexes with reducible substrates S proceed according to two basic soichiometries given in eq 2 and 3. Which of the

$$V^{II}PC + S + 2H^+ \rightarrow V^{IV}PC + SH_2 \quad (2)$$

$$2V^{II}PC + S + 2H^+ \rightarrow 2V^{III}PC + SH_2 \quad (3)$$

stoichiometries is obeyed depends not only on the nature or reactivity of the substrates, but also on the reaction conditions. Equation 2 is valid for easily reducible substrates at high concentrations and eq 3 valid for substrates which are reduced more slowly. However, intermediate situations occur when highly reactive substrates are employed at low concentrations or less reactive substrates at high concentrations, as will be shown below.

Acetylene is reduced to C_2H_4 virtually exclusively. At 1 atm or more, the stoichiometry is that of eq 2; at low concentrations, eq 3 is followed (see Table I).

Evidence for the formation of $V^{IV}PC$ during C_2H_2 reduction was obtained through spectrographic analysis of reaction solutions at t_∞ from reduction experiments at C_2H_2 pressures of 2 atm (Figure 1). In the pH range from 10 to 12.5, which is optimal for N_2 reduction to NH_3, C_2H_2 is reduced virtually exclusively to C_2H_4. Even at low partial pressures of C_2H_2, at best traces of C_2H_6 are formed. Under more strongly alkaline reaction conditions, the reduction of C_2H_2 still produces C_2H_4 as the main product, but small amounts of C_2H_6 are also formed, reaching a maximum of 0.4% relative to C_2H_4 at 0.2 atm of C_2H_2 pressure. C_2H_6 yields decline thereafter, reaching, for example, 0.1% at 1 atm of C_2H_2.

2-Butyne is reduced to *cis*-2-butene at about 10% the rate of C_2H_2 (see Table III). The stereochemical course of the reduction of C_2H_2 is also cis.[7]

Ethylene is reduced slowly to ethane. At low partial pressures of C_2H_4, the stoichiometry of reduction follows eq 3. At high pressures the yields appraoch values between those demanded by eq 2 and 3 (see Table II). It was found that under the conditions used in Table II, with 0.1 atm of ethylene and 10–100 μmol of V(II), the initial rate of ethylene reduction is simply proportional to V(II) concentration.

Table III. Approximate Relative Rates of Reduction of Substrates by $V^{II}PC$ in CH_3OH at 27 °C[b]

no.	substrate	product(S)	relative rates
1	N_2O	N_2, H_2O	1 × 10^4
2	C_2H_2	C_2H_4	4 × 10^3
3	$V^{IV}PC$	$V^{III}PC$	4 × 10^3
4	N_2H_4	NH_3	1 × 10^3
5	$CH_3CH{=}O$	C_2H_5OH	1 × 10^3
6	CO	CH_3OH, $CH_2{=}O$	(ca. 1 × 10^2)[a]
7	N_3	N_2, NH_3	5 × 10^2
8	$CH_3C_2CH_3$	*cis*-$CH_3CH{=}CHCH_3$	3 × 10^2
9	$CH_2{=}O(g)$	CH_3OH	(3 × 10^2)[b]
10	$CH_2{=}CHCH{=}CH_2$	$CH_3CH_2CH{=}CH_2$	2 × 10^2
11	$CH_2{=}O(l)$	CH_3OH	(6 × 10)[c]
12	*n*-C_4H_9Br	*n*-C_4H_{10}	10
13	C_2H_4	C_2H_6	10
14	N_2 (30 atm)	NH_3, (N_2H_4), H_2	10[d]
15	H^+, (CH_3OH)	H_2	1
16	CH_3Cl	CH_4	0.5
17	H^+, (H_2O)	H_2	0.1[e]

[a] Estimated rate corrected for inhibitory effects on the reduction of other substrates. For detection of $CH_2{=}O$ (with chromotropic acid) and of CH_3OH (by GLPC), CO reduction experiments were performed in H_2O as the solvent. [b] For the rate determinations, gaseous $CH_2{=}O$ was injected into the methanolic $V^{II}PC$ solutions. Due to the ease of $CH_2{=}O$ polymerization, rate is not necessarily the true rate of reduction of monomeric $CH_2{=}O$. [c] Rate of reduction as observed with freshly distilled, 37% aqueous formaldehyde solution. [d] Calculated rate of N_2 reduction at 30 atm of N_2, where its concentration in the reaction solution is 0.1 M. [e] Solvent H_2O instead of CH_3OH. [f] Reaction solutions contained at $t = 0$, in a total volume of 5 mL: V(II), 40 μmol; PC, 2500 μmol: $NaOCH_3$, 3000 μmol. Relative rates are expressed for substrate concentrations of 0.1 M with respect to the rate of H_2 evolution from $V^{II}PC$ in the absence of reducible substrates.

Butadiene (1,3) is reduced at about 2% of the rate of C_2H_2 to yield 1-butene. Only traces of butane were detected.

Carbon monoxide was found to be reduced to $CH_2{=}O$ and CH_3OH.[16] It also has a stimulatory effect on the rate of H_2 production. A similar effect has been observed in the V-$(OH)_2$/$Mg(OH)_2$ system[2] and was therefore demonstrated qualitatively.

Formaldehyde reacts with catechol in basic solution to give methylols.[17] However, this reaction is slow compared to the reduction of formaldehyde to methanol and can be neglected. The rate of reaction of formaldehyde with V(II) to yield CH_3OH is strongly dependent on its degree of polymerization. Table III shows that formaldehyde in freshly distilled aqueous solution is reduced at only about one-fifth of the rate with which gaseous formaldehyde is reduced. The rate for "$CH_2{=}O$" reduction is thus difficult to determine accurately. By analogy with acetaldehyde, which is reduced at a rate approaching that of C_2H_2 (see Table III), monomeric formaldehyde in statu nascendi is most likely reduced very rapidly.

Miscellaneous Substrates. Data on the reduction of a number of additional compounds by $V^{II}PC$ are listed in Table III. In all cases the products and stoichiometries observed are consistent with two-electron reductions. The fast rate of reduction of N_2O is particularly noteworthy. Accordingly, its reduction obeys the stoichiometry of eq 2. The related reduction of azide to NH_3 and N_2 is also quite rapid. Alkyl chlorides and bromides are reductively dehalogenated to alkanes at comparatively slow rates. Two examples are given in Table III; the mechanism of these reactions was not investigated.

Spontaneous Hydrogen Evolution. Freshly prepared solutions of $V^{II}PC$ are initially brown but change their color rapidly to green

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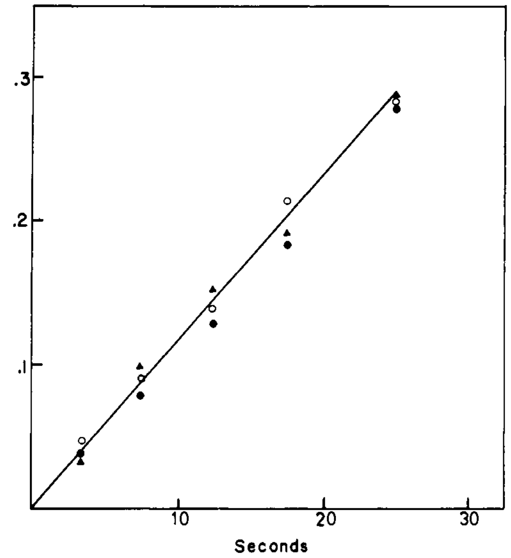

Figure 2. Spontaneous H_2 evolution from $V^{II}PC$ solutions. Plot of $-\ln [V_t/V_0]$ vs. time for three different initial V(II) concentrations: V_0 = initial V(II); V_t equal to V(II) at time t calculated from hydrogen yield at time t and stoichiometry. Catechol was 0.5 M and $NaOCH_3$ 0.6 M in CH_3OH. In total volume of 5 mL, initial V(II) was 8 μmol for data points ○, 32 μmol for ●, and 128 μmol for ▲. Temperature was 0 °C.

Table IV. Dependence of the Initial Rate of H_2 Evolution on the Pyrocatechol Concentration[a]

pyrocatechol concn, M	initial rate of H_2 evolution, $m^2 s^{-1} \times 10^9$	pyrocatechol concn, M	initial rate of H_2 evolution, $m^2 s^{-1} \times 10^9$
0.05	4.3	0.20	73
0.10	18	0.40	300

[a] Above reaction solutions contained 40 μmol of V(II) in a total volume of 5 mL of CH_3OH. $NaOCH_3$ concentration equal to 1.5 times catechol concentration. Temperature at 0 °C. Initial rate for first 20 s of reaction.

within seconds after mixing. From such solutions, hydrogen evolves according to eq 4. The kinetics of reaction 4 are complex

$$2V^{II}PC + 2H^+ \rightarrow 2V^{III}PC + H_2 \qquad (4)$$

and exhibit in part autocatalytic behavior.

Because of the complexity of the system, only some of the more important features of the reaction will be reported. First and foremost, it is found that the initial rate of H_2 evolution depends linearly on the V(II) concentration (see Figure 2). Moreover, Table IV indicates a second-order dependence of the initial rate of H_2 evolution on catechol concentration, suggesting that one V(II) ion and two pyrocatechol ligands are present in the active complex for H_2 evolution.

To establish the dependence of H_2 evolution on the concentration of H^+ ions in the reaction solution, we made measurements at different molar ratios of base to catechol, in CH_3OH, H_2O, or D_2O. At the molar 1:1 ratio in CH_3OH, the effective pH of the solutions was measured as 11.7 with pH-indicating dyes. Below the 1:1 ratio, the rate of H_2 evolution is inversely proportional to the H^+ concentration. Above this ratio or pH 11.7, the rate is virtually independent of H^+ concentration (see Table V). In the region in which the rate is inversely proportional to $[H^+]$, the evolution of D_2 from D_2O occurred at an initial rate ca. 0.5 that of the evolution of H_2 from H_2O. In the H^+-independent region, no kinetic isotope effect was observed.

Measurements of the solution pH before and after H_2 evolution revealed changes no greater than 0.1 pH unit. This is because alkaline solutions of pyrocatechol are effectively buffered due to the acidic nature of this phenol derivative (pK_1 of PC = 9.4; pK_2 = 12.9).[18]

Table V. Dependence of the Initial Rate of H_2 Evolution on Hydrogen Ion Concentration[a]

molar ratio $NaOCH_3$:PC	effective pH	$1/H^+$, $mL^{-1} \times 10^{-10}$	initial rate of H_2 evolution, $m^2 s^{-1} \times 10^9$
0.43	9.9	0.79	3.2
0.67	10.6	4.0	15
0.85	11.6	40	160
1.0	11.8	63	220
1.22	12.0	100	380
2.0	12.4	250	400

[a] Above reactions contained 2500 μmol of catechol, $NaOCH_3$ as indicated, 40 μmol of V(II), in 5.0 mL of CH_3OH. Temperature at 0 °C. Initial rate for first 20 s of reaction.

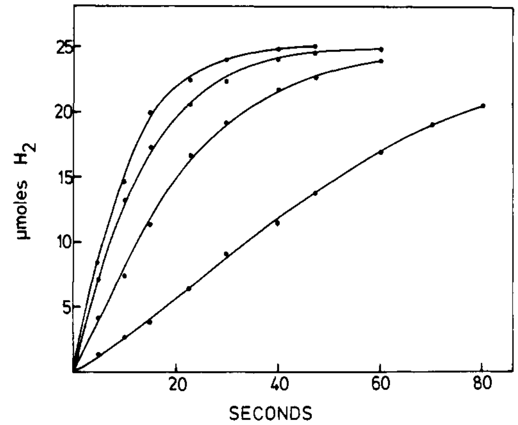

Figure 3. Autocatalysis of H_2 evolution by V(III): time dependence of H_2 evolution as a function of added V(III). Solid points are the observed H_2 yields. Solid curves were calculated from the integrated form of the standard autocatalytic rate equation $dX/dt = k_1(A - X) + k_2(A - X)(B + X)$, with appropriately selected values of k_1, k_2, A, and B, where A and B are the initial amounts of V(II) and V(III) and X is the amount of V(II) consumed at time t. All reactions were run at 0 °C, with 2500 μmol of PC, 8000 μmol of $NaOCH_3$, 50 μmol of V(II), in a total volume of 5 mL. The V(III) was added in the form of the chloride, in amounts of 150, 100, 50, and 0 μmol, respectively, going from the top to the bottom curves.

As shown in Figure 3, added V(III) stimulates H_2 evolution in the $V^{II}PC$ system. This autocatalytic effect of V(III) on H_2 evolution is comparatively weak and is observed only at high V(III) concentrations. Similarly, only a minor effect of V(III) on the rate of H_2 production was observed at short times and low initial V(II) concentrations. Thus, initially, the H_2 evolutions is simply first order in V(II), as shown in Figure 2.

At the low N_2 pressures employed, the autocatalytic stimulation of the rate of hydrogen production causes a significant decrease in the production of NH_3 relative to H_2 in the later phases of the reaction (see Table VII). Under optimal conditions for NH_3 production at 1 atm of N_2 pressure (see entry no. 14, Table VII), the yield of NH_3 in the presence of added V(III) was significantly lower than without added V(III). Because of V(III) autocatalysis of H_2 production, the relative rates of H_2 evolution in Table III are given for the initial phases of the reaction where the concentration of V(III) is still very low and autocatalytic effects are small.

Reduction of Molecular Nitrogen. The reduction of N_2 with $V^{II}PC$ to NH_3 in CH_3OH occurs optimally only in a very narrow effective pH range, corresponding to an aqueous pH of about 10–12.5; a similar pH optimum was observed by Nikonova et al.[7] in aqueous solution. In Figure 4, the dependence of the yields of NH_3 on the pH or alkalinity of the reaction solutions is shown. In addition, the H_2 yields are shown and it may be verified that the sum of reducing equivalents consumed for H_2 and NH_3

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(18) Jameson, R. F.; Wilson, M. F. *J. Chem. Soc. Dalton Trans.* **1972**, 2610.

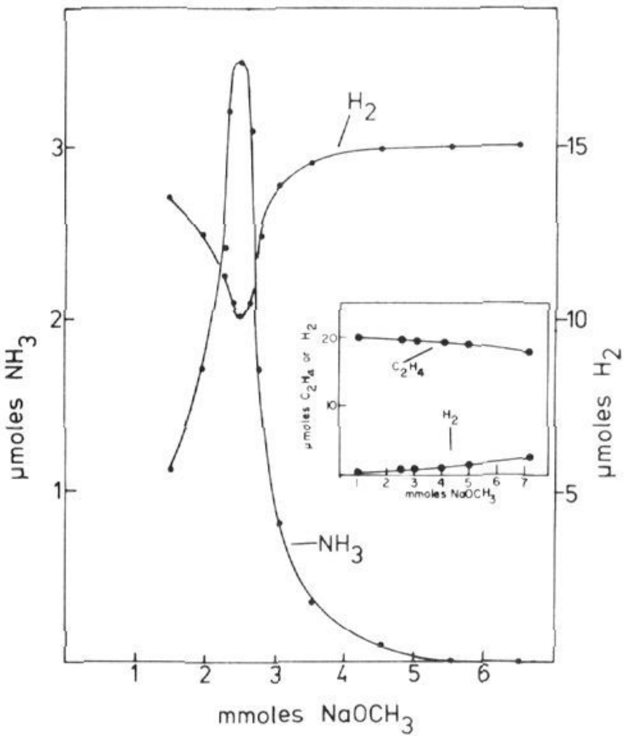

Figure 4. Alkalinity vs. yield profiles for NH_3 and H_2 formed in the reduction of N_2 by $V^{II}PC$ in methanol at 25 °C. Reaction solutions contained initially, in a total volume of 5 mL, 2500 µmol of catechol, $NaOCH_3$ as indicated, and 30 µmol of V(II). Yields are for t_∞ and 1 atm of N_2. Inset shows results under same conditions except 60 µmol of C_2H_2 used as substrate.

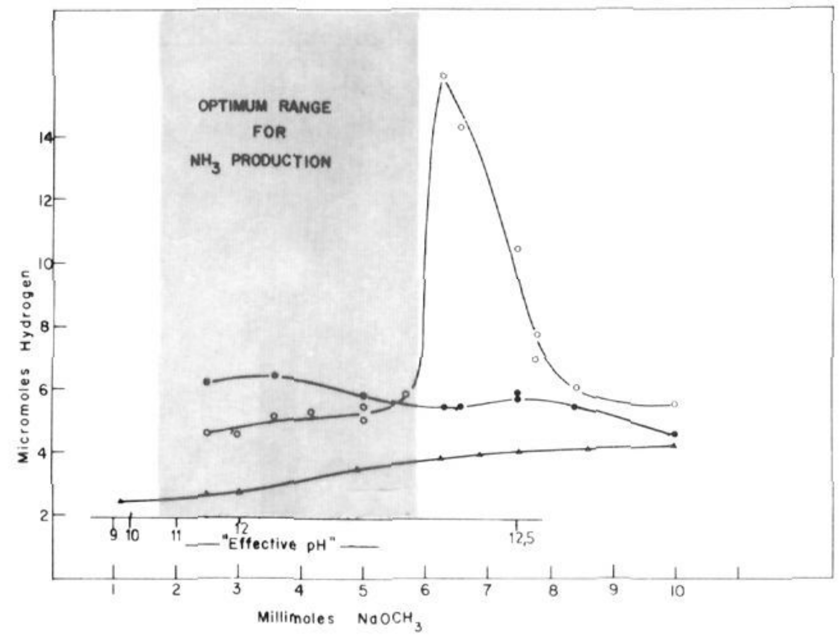

Figure 5. Hydrogen yield vs. alkalinity (pH) after 30 s of reaction. Reactants are as in Figure 3. Data points: O for 1 atm of N_2; ● for argon; ▲ for C_2H_2, 1 cm^3. All measurements at 20 °C. Note stimulation of hydrogen by nitrogen at higher than optimum alkalinity for NH_3 production.

Table VI. Inhibition of H_2 Evolution by Allyl Alcohol in the Presence and Absence of N_2[a]

µmol of allyl alcohol needed to effect 50 or 75% inhibiton		% inhibition of H_2 evolution
argon	nitrogen	
25	10	50
100	30	75

[a] Reaction solutions contained, in a total volume of 5 mL, at $t = 0$: V(II), 42 µmol; PC, 2500 µmol; $NaOCH_3$, 2800 µmol. Yields of H_2 measured after 1 min at 27 °C.

production corresponds to the quantitative oxidation of $V^{II}PC$ to $V^{III}PC$. As can be observed from the inset in Figure 4, C_2H_2 does not exhibit such a pH dependence but rather is reduced almost independently of base concentration.

Since N_2H_2 is decomposed in alkaline media into N_2 and H_2, we followed the H_2 evolution after short reaction times as a function of the pH or alkalinity of the reaction solutions. Figures 5 and 6 reveal a significant N_2-dependent H_2 production above the optimal pH for NH_3 production. This behavior is observed only for N_2. The results under argon and in the presence of C_2H_2 are included in Figure 5 for comparison. With water as a solvent, an increase in the initial rate of H_2 evolution was observed which was linear with N_2 pressure (see Figure 7). No NH_3 was detected under these conditions.

Allyl alcohol was found to inhibit H_2 evolution in the presence of nitrogen as a substrate 3 times more effectively than the hydrogen evolution under argon (see Table VI).[19] Under the same

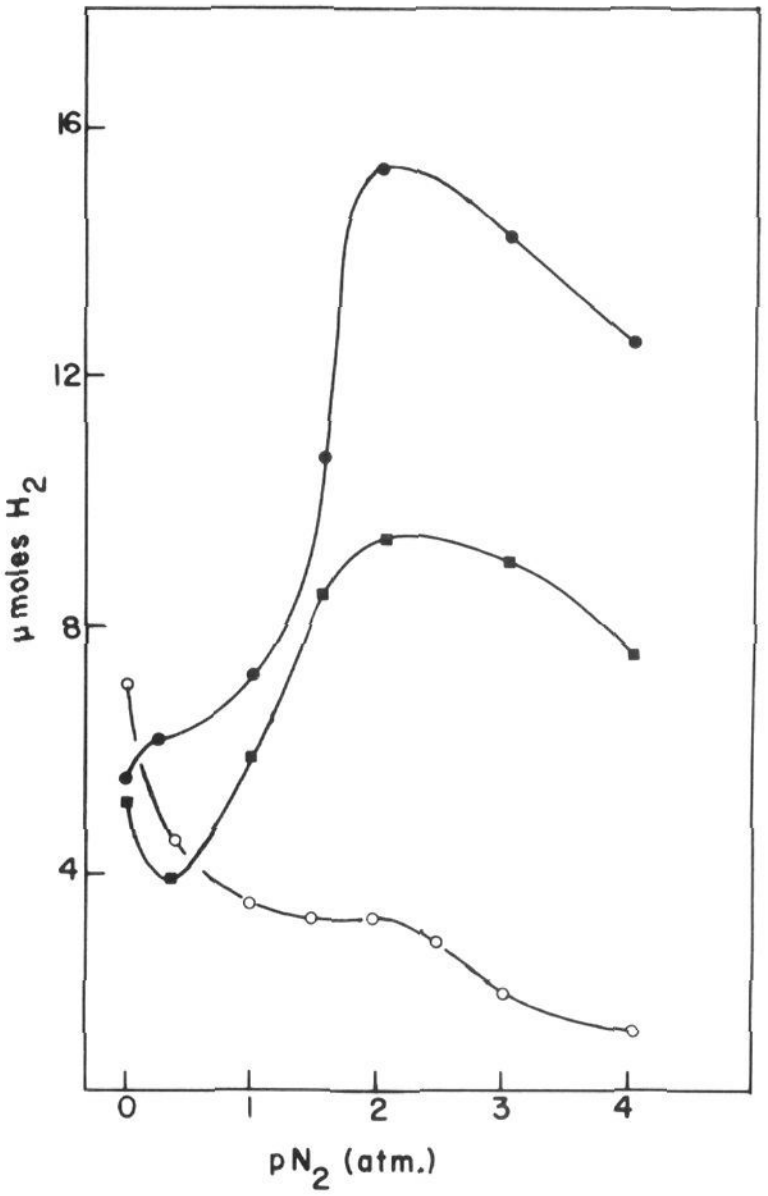

Figure 6. Hydrogen yields after 30 s of reaction vs. N_2 pressure at three different alkalinities. In each case reaction solution volume was 5 mL, containing 50 µmol of V(II) and 2500 µmol of catechol. $NaOCH_3$ was 2700 µmol for data points (O), 5000 µmol for (■), and 7500 µmol for (●). Temperature was 20 °C and N_2 pressure as indicated.

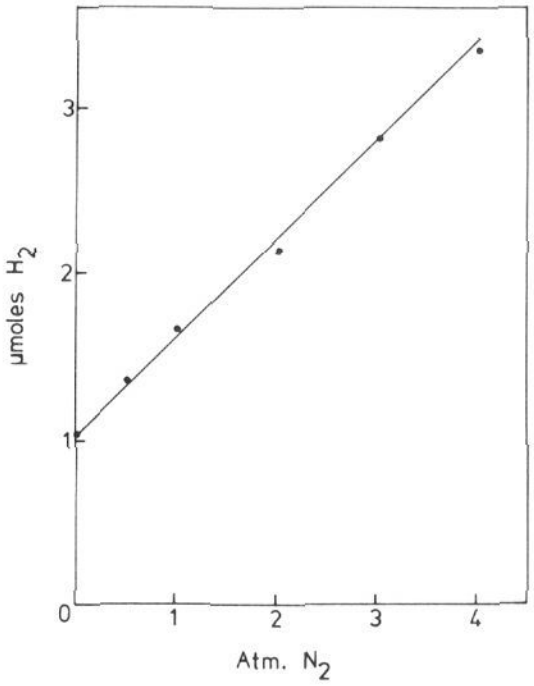

Figure 7. Stimulation of H_2 evolution by N_2 with H_2O as the solvent. H_2 evolved at 30 s plotted vs. N_2 pressure. All reactions were in H_2O at 20 °C with 2500 µmol of PC, 2500 µmol of NaOH, and 30 µmol of V(II), all in 5 mL total volume.

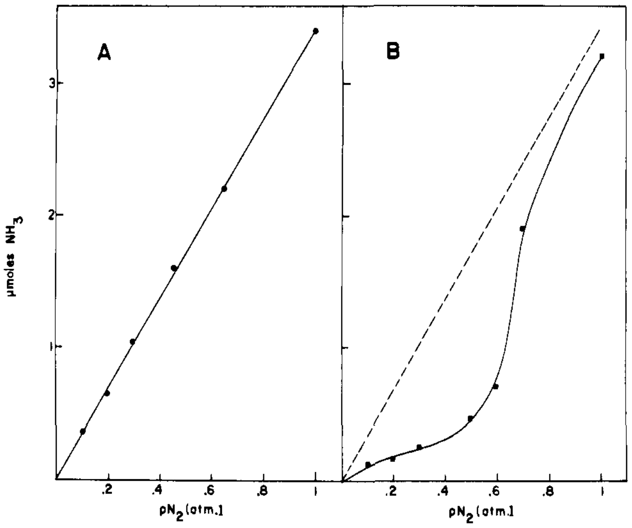

Figure 8. Ammonia yields vs. N_2 pressure at A, the optimum base concentration, and B, slightly higher than optimal base concentration. In all cases, total volume was 5 mL, containing 30 μmol of V(II), 2500 μmol of catechol. In A total $NaOCH_3$ was 2500 μmol and in B it was 2800 μmol. Temperature was 20 °C.

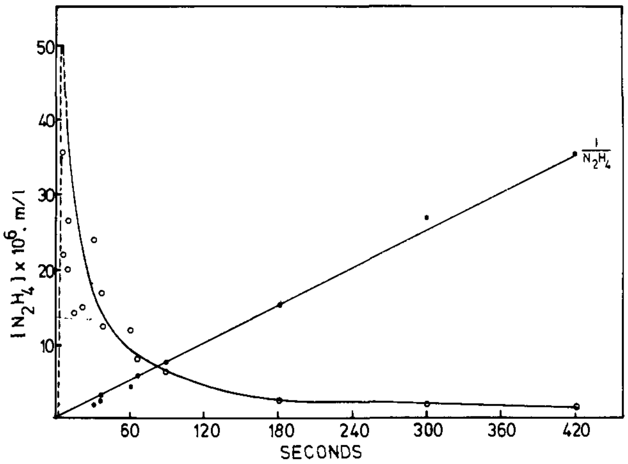

Figure 9. Accumulation and disappearance of N_2H_4 from N_2 reduction experiments with $V^{II}PC$ at 100 atm of N_2 pressure. Adapted from ref 10, loc. cit. The experimental points were fit to the equation $[N_2H_4]^{-1} = at + b$, consistent with a second-order disappearance ($r = 0.99$, $P < 0.001$) and a mechanism involving the formation and disproportionation of N_2H_2 under the reaction conditions.

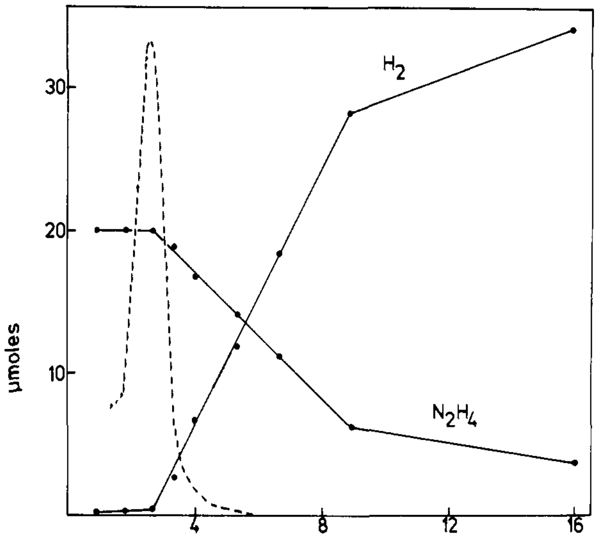

Figure 10. Decomposition of thermally generated N_2H_2 as a function of base concentration. Solutions contained 2500 μmol of catechol, $NaOCH_3$ as indicated, and 40 μmol of tosyl hydrazide in 5 mL total volume of CH_3OH. Solutions heated under Ar for 24 h at 85 °C. Yields of H_2 and N_2H_4 then were measured. Dotted line indicates 10 × NH_3 yields in Figure 4.

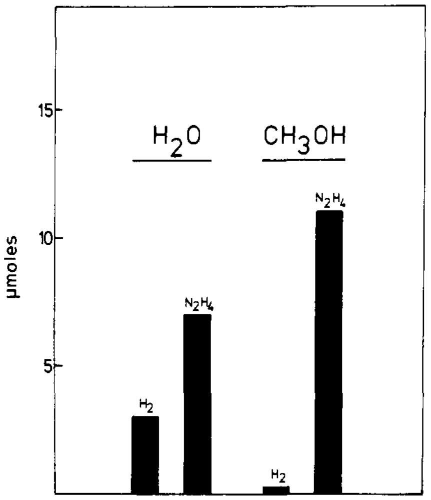

Figure 11. Products from reaction of thermally generated N_2H_2 in H_2O vs. CH_3OH. Solutions contained 2500 μmol of catechol and of base in a total of 5 mL of H_2O or CH_3OH, as indicated. Each contained 50 μmol of tosyl hydrazide and was heated at 85 °C under Ar for 24 h.

conditions only 3 μmol of allyl alcohol caused a 50% inhibition of the NH_3 yield under 1 atm of N_2 pressure. The yields of NH_3 increase linearly with $p(N_2)$ at the optimal pH for NH_3 production. At higher pH, a nonlinear dependence is observed (see Figure 8).

In Table VII, the results of N_2 reduction experiments are summarized. The first six experiments listed show that NH_3 production relative to H_2 evolution drops off in the later phases of the reaction. Experiments 7–11 indicate the strong pH dependence of the ammonia yield. Experiments 12–16 illustrate the dependence on V(II), experiments 17–22 show the dependence on N_2 pressure, and experiments 23–28 show the temperature dependence.

Hydrazine was not detectable under our experimental conditions but has been observed in reactions at high N_2 pressures after short reaction times.[10] Table III shows that hydrazine is reduced about 100 times more rapidly than N_2 and thus cannot accumulate appreciably in experiments at low or high N_2 pressures. The fact that N_2H_4 has been observed in quenching experiments[10] at high nitrogen pressures is consistent with the intermediacy of diimide, as will be outlined in the Discussion (see Figure 9).

In Situ Generation of N_2H_2. The base-catalyzed decomposition of diimide thermally generated from benzene sulfonyl hydrazide[20] was found to begin at precisely the pH at which the ammonia yield in the reduction of N_2 begins to decline (see Figure 10). Traces of O_2 and V(III) concentrations equivalent to those encountered in our nitrogen reduction studies had no substantial effect on the fate of the thermally generated diimide. At the optimum pH for N_2 reduction, the yield of H_2 vs. N_2H_4 was 15 times greater in H_2O than in CH_3OH (see Figure 11).

Discussion

Reduction of Substrates Other than Nitrogen. Complexes of vanadium (II) with pyrocatechol are some of the most powerful reducing substances known. Our work indicates that they behave

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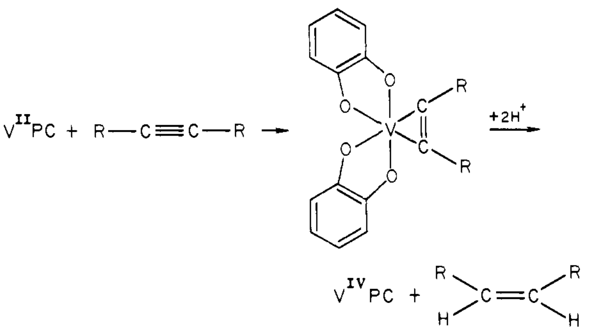
(19) Allyl alcohol is reduced to propanol by $V^{II}PC$ rapidly; hence no differences in the yields of propanol generated under argon or nitrogen can be observed. In the $V(OH)_2/Mg(OH)_2$ system, a stimulation of propanol production by N_2 occurs after short reaction times and was ascribed to the presence of diimide. The t_∞ yields of propanol are identical in reactions under argon or nitrogen as allyl alcohols is also reduced, albeit more slowly than by diimide, by $V(OH)_2/Mg(OH)_2$.

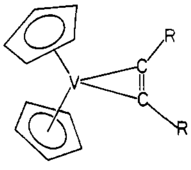
(20) Hünig, S.; Müller, H. R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 214.

as two-electron reductants in reactions with a variety of substrates. Acetylene is reduced to ethylene. The reduction occurs stereospecifically cis.[7] 2-Butyne is similarly reduced to cis-2-butene. Hence, the reduction must occur through a "side-on" interaction of the substrate with the reactive $V^{II}PC$ complex and may be formulated as shown in eq 5. The presence of two PC ligands was demonstrated in the case of H_2 evolution by the method of initial rates (see Table IV).



(5)

The intermediate organovanadium(IV) complex is plausibly assumed to be pseudooctahedral in the light of recent X-ray crystallographic evidence which indicates that vanadium(IV)-pyrocatechol complexes are octahedral[21] rather than tetrahedral.[22] That alkynes can form side-on complexes with V(II) has recently been demonstrated in studies of the reaction of alkynes with dicyclopentadienylvanadium(II), affording complexes of the type A.[23] The lability of V–C σ bonds in protic media precludes the isolation of analogous complexes in the $V^{II}PC$ system.



A

Since C_2H_2 can be reduced quantitatively to C_2H_4 and no evidence for a direct reduction of C_2H_2 to C_2H_6 was obtained even under conditions which favor C_2H_6 production, mechanisms invoking dimeric or tetrameric $V^{II}PC$ clusters as four-electron reducing agents need no longer be considered.

Mechanisms analogous to that shown in eq 5 are proposed for the reduction of olefinic substrates. Because of their low reactivities, $V^{III}PC$ is formed since $V^{IV}PC$ can react with remaining $V^{II}PC$. However, even with C_2H_4 the stoichiometry of eq 2 is approached at sufficiently high substrate concentrations.

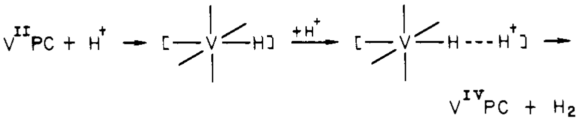
The reduction of N_2O to N_2 and H_2O and the reduction of azide to N_2 and NH_3 are typical two-electron reduction processes, as is the reductive dehalogenation of alkyl halides. These reactions have been shown[1,2,24] to occur in the $V(OH)_2/Mg(OH)_2$ or molybdothiol systems and will not be discussed here.

The finding that even carbon monoxide is reduced[16] attests the powerful reducing properties of $V^{II}PC$. It would seem unlikely that CH_3OH is formed from CO in one step. A plausible mechanism via formaldehyde as the intermediate can be formulated; however

$$V^{II}PC + CO \rightarrow V(CO)PC \xrightarrow[-V^{IV}PC]{+2H^+} CH_2{=}O \xrightarrow[-V^{IV}PC]{+2H^+,\ V^{II}PC} CH_3OH \quad (6)$$

The authors of ref 16 initially rejected a two-step mechanism mainly because formaldehyde was apparently reduced too slowly to qualify as an intermediate. Our experiments indicate that the rate of reduction of formaldehyde by $V^{II}PC$ depends greatly on its state of aggregation. In aqueous solution, even if it is freshly distilled, formaldehyde is reduced much more slowly that if it is first generated in the gaseous state and injected into the reaction solution (see Table III). Truly monomeric $CH_2{=}O$ as generated under the conditions of CO reduction would probably be reduced very rapidly indeed. An indication for this is the high rate of reduction observed for acetaldehyde (see Table III).

Spontaneous Hydrogen Evolution. Reduction of solvent protons to H_2 occurs in the absence of added reducible substrates. Figure 2 shows that the reaction is first order in V(II) and hence must occur in at least two steps. In the first step, H_2 is probably formed via an intermediate hydridovanadium species. We favor an ionic reaction as shown in eq 7 over a homolytic mechanism involving the combination of two H atoms. In the second step, the $V^{IV}PC$ generated reacts with remaining $V^{II}PC$ to yield $V^{III}PC$ according to eq 8. Table III indicates that reaction eq 8 is fast, and hence the formation of $V^{III}PC$ can be suppressed effectively only during the reduction of the most reactive substrates at high concentrations.

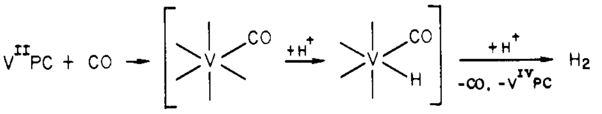


(7)

$$V^{IV}PC + V^{II}PC \rightarrow 2V^{III}PC \quad (8)$$

The autocatalytic effect of V(III) on H_2 production in the absence of added reducible substrates as shown in Figure 3 complicates the mechanism but is important only at high V(III) concentrations. The effect is furthermore negligibly small during the early phases of the reaction.

The spontaneous H_2 evolution is not inhibited by CO. It is instead stimulated, just as has been observed in the $V(OH)_2/Mg(OH)_2$ system.[2] This effect is attributed to the formation of a CO adduct of $V^{II}PC$ which still contains a free coordination site for protonation and yields H_2 via an intermediate hydride according to eq 9.



(9)

Reduction of Molecular Nitrogen. The present study offers several salient points of evidence in favor of a stepwise mechanism of N_2 reduction in the $V^{II}PC$ system. They are based on: interpretation of the pH and solvent dependence of N_2 reduction, the anomalous N_2 dependent H_2 evolution in alkaline solutions, and direct observations on the behavior of diimide generated thermally from tosyl hydrazide.[20] Diimide may be logically expected as the first product of N_2 reduction in the $V^{II}PC$ system if only because C_2H_2 is also only reduced to the two-electron reduction product, ethylene. However, while C_2H_4 is thermodynamically stable and, under appropriate conditions, is reduced further to C_2H_6, N_2H_2 is thermodynamically and kinetically unstable, undergoing either disproportionation into N_2 and N_2H_4 or decomposition into the elements.

Diimide decomposition and disproportionation are competitive processes. The decomposition into the elements, also known as "Raschig decomposition", is base catalyzed and formulated in eq 10.[25] The decomposition of N_2H_2 is also favored over the disproportionation if it is generated at very low stationary concentrations. Thus, "anomalous" H_2 evolution may be encountered whenever diimide is generated above a certain optimal pH or at low concentrations.

$$N_2H_2 \xrightarrow[-HB]{+B^-} [H\text{-}N_2]^- \xrightarrow[-N_2]{} [H^-] \xrightarrow[-B^-]{+BH} H_2 \quad (10)$$

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[21] Copper, S. R., personal communication, 1980.

[22] Wilshire, J. P.; Sawyer, D. T. *J. Am. Chem. Soc.* **1978**, *100*, 3972.

[23] Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1979**, *18*, 2282.

[24] See: Schrauzer, G. N. *Angew. Chem.* **1975**, *87*, 579; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 514.

[25] Hünig, S.; Müller, H. R.; Thier, W. *Angew. Chem.* **1965**, *77*, 368; *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 271.

Table VII. Yields of Ammonia from Reactions of Nitrogen with $V^{II}PC$ Complexes under Various Experimental Conditions

no.	variable	initial V(II)	concn,[a] M PC	concn,[a] M $NaOCH_3$	$p(N_2)$, atm	*t*, s	yield of NH_3	μmol of H_2
1	time	0.006 (30)	0.5	0.5	1	10	1.2	0.90
2						30	2.1	4.5
3						60	3.0	8.1
4						90	3.4	9.1
5						300	3.5	9.5
6						600	3.5	9.5
7	$[NaOCH_3]$	0.006 (30)	0.5	0.30	1	*b*	1.1	13.4
8				0.45			2.4	11.4
9				0.50			3.5	9.8
10				0.55			1.7	12.5
11				0.70			0.3	14.6
12	[V(II)]	0.0035 (17.5)	0.5	0.5	1	*b*	1.0	7.2
13		0.0070 (35)					4.0	11.5
14		0.010 (50)					6.3	15.6
15		0.014 (70)					7.4	24
16		0.024 (120)					8.0	48
17	$p(N_2)$	0.006 (30)	0.5	0.5	0.1	*b*	0.35	14.5
18					0.2		0.66	14
19					0.3		1.10	13
20					0.46		1.65	12.5
21					0.65		2.26	11.5
22					1.00		3.5	10
						temp,[b] °C		
23	temp	0.006 (30)	0.5	0.55	1	0	0.7	14
24						25	1.5	13
25						50	3.8	9.3
26						70	6.0	6
27						100	2.0	12

[a] Under standard experimental conditions as outlined in Experimental Section. Total amounts of V(II) (μmol) in parentheses. Total solution volume 5.0 mL. Temperature at 20 °C except as noted. [b] Measured at t_∞.

Figure 4 shows that the NH_3 is produced only within a narrow pH range, with a sharp optimum at pH 11.7. Above this pH, the yields of NH_3 decline sharply. This extreme pH dependence in the reduction of N_2 is in sharp contrast to the virtual pH independence of C_2H_2 reduction in the same pH range. (see insert, Figure 4). The anomalous features of N_2 reduction in this system can be interpreted on the basis of the known properties and reactions of N_2H_2. The initial increase of the NH_3 yields with increasing pH is attributed to the increase of the reducing potential of V(II) and its PC complexes. Although the instability of $V^{II}PC$ complexes has thus far precluded measurements, data for $V(OH)_2$ are available[26] which indicate a substantial increase of the reduction potential in the pH range between 9 and 11. For N_2H_2 to be generated from N_2, the reduction potential must be in the order of at least -1.1 V.[27] For C_2H_2 reduction, a lower potential suffices, and thus its reduction to C_2H_4 in the $V^{II}PC$ system is possible even at comparatively low pH. However, the yields of NH_3 in the reduction of N_2 demonstrate a sharp decline above pH 11.7. This is attributed to beginning base catalysis of N_2H_2 decomposition. Above the optimal pH for N_2 reduction an N_2-dependent evolution of H_2 is observed, which is also in accord with the expected behavior of N_2H_2 under conditions of Raschig decomposition (Figure 5). Figures 6 and 7 show that the evolution of H_2 in alkaline solution increases with increasing N_2 pressure. In CH_3OH as the solvent, a maximum of the H_2 evolution is osbserved at an intermediate N_2 pressure. The decline at higher N_2 pressures occurs because N_2H_2, now generated in higher stationary concentrations, disproportionates to N_2 and N_2H_4 with higher efficiency[28] (Figure 6).

In H_2O as the solvent, at the optimal pH for N_2 reduction, a N_2-stimulated evolution of H_2 is observed at low N_2 pressures which is linear with $p(N_2)$ in the range between 0 and 4 atm (Figure 7), and only traces of NH_3 are formed. Under these conditions, virtually all the N_2H_2 generated is lost through decomposition into the elements. At high N_2 pressures (i.e., 100 atm), disproportionation of N_2H_2 becomes the main reaction, as evidenced by the significant yields of NH_3 which have been observed under these conditions.[6] The Russian workers attributed the lower yields of NH_3 in H_2O as compared to CH_3OH to the greater tendency of $V^{II}PC$ complexes to decompose with H_2 evolution in water.[6] However, our data in Table III show that the rate of H_2 evolution from aqueous $V^{II}PC$ solutions under *argon* is in fact slower than in CH_3OH as the solvent.

Suspecting that the solvent dependence of NH_3 production may reflect reactivity differences of N_2H_2, we decided to investigate the behavior of *thermally* generated N_2H_2 under conditions of N_2 reduction in the $V^{II}PC$ system. Figure 11 shows that *much larger amounts of H_2 relative to N_2H_4 are formed in H_2O than in CH_3OH*, indicating that N_2H_2 prepared from tosyl hydrazide also decomposes to a greater extent in H_2O than in CH_3OH under otherwise identical conditions. Thermally generated N_2H_2 (from tosyl hydrazide) also begins to suffer Raschig decomposition at the same pH at which the decline of the NH_3 yields in N_2 reduction experiments is observed (see Figure 10).

Since allyl alcohol is easily reduced by N_2H_2,[19,29] its addition to reacting $V^{II}PC$ systems in the presence of N_2 has a significantly greater inhibitory effect on H_2 production than under argon (Table VI). Allyl alcohol also has an inhibitory effect on NH_3 production which is greater than could be accounted for by mere competition of allyl alcohol with N_2 for $V^{II}PC$.

That N_2 is reduced consecutively via diimide and hydrazine is indicated by experiments which show that N_2H_4 is detectable in reactions of $V^{II}PC$ with N_2 at high pressures and after short reaction times.[10] The Russian workers[10] suggested that the N_2H_4

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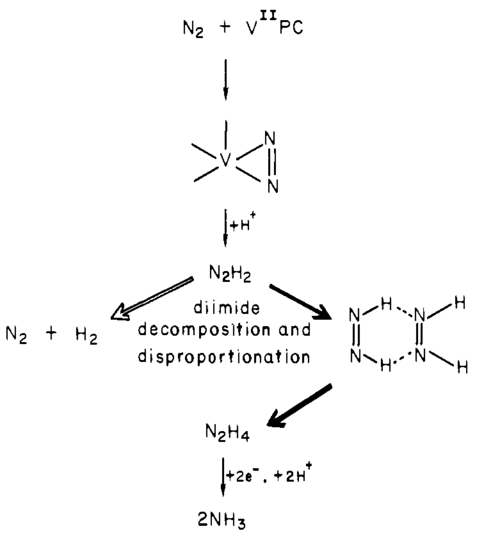
(26) M. Pourbaix, "Atlas of Electrochemical Equilibria in Aqueous Solution"; Pergammon Press: New York, 1966; p 237.

(27) Shilov, A. E. *Russ. Chem. Rev. (Engl. Transl.)* **1974**, *43(5)*, 378.

(28) The effect on NH_3 yield of increasing nitrogen pressure at higher than optimum alkalinity can be seen in Figure 8B. At low N_2 pressure almost no NH_3 is formed due to diimide decomposition. The yield increases approximately as the square of $p(N_2)$, however, due to the second-order disproportionation reaction until a region is reached where the second order reaction predominates. Then, as for the optimal alkalinity in Figure 8A, decomposition is minimized.

(29) van Tamelen, E. E.; Dewey, R. S.; Timmons, R. J. *J. Am. Chem. Soc.* **1961**, *83*, 3725.

Scheme I



is the product of hydrolysis of an intermediate complex. They also argued that N_2H_4 is formed outside the main path of N_2 reduction to NH_3. Assuming that N_2 is reduced directly to NH_3, they concluded that only 1% of the N_2 is reduced via N_2H_4.[10]

The experiment from ref 10 is reproduced in Figure 9. *It is actually a diimide-trapping experiment*, and the observed results can be taken as a proof for the diimide mechanism of N_2 reduction proposed by us. It must first be mentioned that N_2H_4 is reduced ca. 100 times more rapidly than N_2 (see Table III) and that N_2H_4 therefore cannot accumulate in *reacting* solutions under any conditions.

However, if the reactions are stopped with acid, the N_2H_2 present in the solution at this moment can still disproportionate into N_2H_4 and N_2. Accordingly, the amounts of N_2H_4 detected at various time points are a measure of the stationary N_2H_2 concentration. The shape of the N_2H_4 disappearance function in Figure 9 indicates that N_2H_4 is the product of a second-order reaction. This result is typical for the kinetic behavior of N_2H_2 under conditions where its disproportionation into N_2H_4 and N_2 is the main reaction.[1,30]

We thus conclude that the "diimide mechanism" of N_2 reduction as proposed[1,2,24] from studies in the $V(OH)_2/Mg(OH)_2$- and molybdothiol systems (Scheme I) also applies to the reduction of N_2 by $V^{II}PC$.

Acknowledgment. This work was supported by Grants CHE76-10890 and CHE79-50003 from the National Science Foundation. We thank Craig Martin, Keith Pence, and Robert Deere for skillful experimental assistance.

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Ferric Ion Sequestering Agents. 6.[1] The Spectrophotometric and Potentiometric Evaluation of Sulfonated Tricatecholate Ligands

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Abstract: Ferric ion complexation equilibria have been evaluated for the sulfonated tricatecholate ligands 1,3,5-tris[((2,3-dihydroxy-5-sulfobenzoyl)amino)methyl]benzene (MECAMS), 1,5,10-tris(2,3-dihydroxy-5-sulfobenzoyl)-1,5,10-triazadecane (3,4-LICAMS), 1,5,9-tris(2,3-dihydroxy-5-sulfobenzoyl)-1,5,9-cyclotriazatridecane (3,3,4-CYCAMS), and 1,3,5-tris[(2,3-dihydroxy-5-sulfobenzoyl)carbamido]benzene (TRIMCAMS). Protonation and formation constants have been determined by potentiometric and spectrophotometric techniques. The formation constants show that these ligands form exceptionally stable complexes with ferric ion ($\log K_{ML} \approx 40$). The protonation studies have established that the complexes of MECAMS, 3,4-LICAMS, and 3,3,4-CYCAMS undergo a series of 1:1 protonation reactions which result in a shift in the mode of bonding from one in which the iron(III) is coordinated through the two phenolic oxygens of the dihydroxybenzoyl group (catecholate mode) to one in which the meta phenolic group is protonated and the iron(III) is bound through the ortho phenolic and amide carbonyl oxygens (salicylate mode). The results are discussed in relation to the chelation therapy of iron overload, as occurs in the treatment of Cooley's anemia.

The average adult contains 4–5 g of elemental iron, of which about 65% is present in the oxygen-transport protein hemoglobin and another 30% is stored in the iron-storage proteins ferritin or hemosiderin.[2] The transport of iron and the maintenance of free ferric ion concentrations at a low equilibrium value are accomplished by the iron-transport protein transferrin. However, despite the human body's ability to manage relatively high levels of iron, excessive amounts of this element are in fact quite toxic. Indeed, with the advent of iron-enriched vitamin supplements, acute iron overload has become one of the most common types of poisoning among young children.[3] Acute poisoning of adults is less common, but chronic iron overload is frequently encountered as a side effect of the regular transfusions of whole blood required by individuals suffering from β-thalassemia, a genetic disease characterized by the deficient production of the β chains of hemoglobin.[4] Such transfusions are necessary to maintain adequate hemoglobin levels—but since the body has no effective mechanism for excreting

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[1] Part 5 in this series: Weitl, F. L.; Raymond, K. N.; Durbin, P. W. *J. Med. Chem.* **1981**, *24*, 203–206.

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