

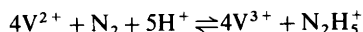
## Nitrogen Fixation. I. Synthesis of Hydrazine from Molecular Nitrogen by Transition Metal Complexes

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Several systems of vanadium(II) ions and various oxygen-containing ligands have been tested for their capacity to catalyze the reduction of molecular nitrogen to hydrazine. The ligands have been selected so that the distance between two vanadium atoms in a bi- or multinuclear complex should be such that a V–N<sub>2</sub>–V bridge could be formed. In this way the symmetric attack on the N<sub>2</sub> molecule is facilitated. The most effective ligand-metal ion combination was found to be  $\alpha,\omega$ -dicarboxylates and V<sup>2+</sup> in proportion 2:3 at a pH of about 4.5. The highest yield of N<sub>2</sub>H<sub>4</sub> was found for <sup>-</sup>OOC–(CH<sub>2</sub>)<sub>n</sub>–COO<sup>-</sup> with n=5 or 6.

The yield corresponds very closely to the equilibrium position of the reaction



As the equilibrium is reached the ligands are thus good catalysts for the above reaction. A complete catalytic process from N<sub>2</sub> to N<sub>2</sub>H<sub>4</sub>, however, must include the reduction of vanadium(III) to vanadium(II).

Also other systems showed catalytic activity, *e.g.* polycarboxylates formed by copolymerization of styrene and cinnamic acid or acrylic acid, respectively. It is suggested that in these polymers the carboxylate groups are statistically distributed so that a suitable V–N<sub>2</sub>–V bridge can be formed.

The last decade has seen an intensive activity in the field of nitrogen fixation. Two discoveries have contributed to this. The first one was the demonstration by Volpin and coworkers<sup>1</sup> that it was possible to synthesize ammonia from the elements H<sub>2</sub> and N<sub>2</sub> in solutions containing transition metal compounds. The other discovery was the synthesis of dinitrogen complexes of transition metal ions by Allen and Senoff.<sup>2</sup> These discoveries seemed to

open new routes for the synthesis of nitrogenous compounds, in the first place ammonia and hydrazine, from molecular nitrogen and under mild conditions. Several reviews on the subject have appeared.<sup>3–7</sup> The advances made in the characterization of nitrogen fixing enzymes<sup>8</sup> have also encouraged further research on non-biological analogues.

Part of the work has concerned the physico-chemical characterization of the dinitrogen complexes, of which now a considerable number is known. Another part has been devoted to searching for systems that would work catalytically in the reduction of dinitrogen. Such systems have mainly been constructed from organic solvents and Lewis acid compounds, such as, *e.g.*, Volpins<sup>1</sup> original one (Al, AlBr<sub>3</sub>–TiPr<sub>4</sub>–ether) or van Tamelen's<sup>9</sup> [Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>–Al(i-PrO)<sub>3</sub> Na<sup>+</sup> Np<sup>-</sup> or Al(anode)]. Some investigators, however, have deliberately tried to use aqueous systems, thus approaching the route that Nature has selected for nitrogen fixation. The work of Schrauzer *et al.*<sup>10</sup> (Mo(III), Fe(II), sulfur compounds and reducing agents) and of Shilov and coworkers<sup>11</sup> (Ti(III), Mo(III)/V(II) in alkaline solution containing Mg-salts) are the most prominent.

The latter work<sup>11</sup> has been a stimulus to us in our studies on the synthesis of hydrazine. Shilov notes that hydrazine is formed as the reduction product of dinitrogen and that the presence of magnesium salts is necessary for a good yield. Basing his reasoning on these two facts, Shilov suggests a mechanism for the reaction involving a bridged structure in which the N<sub>2</sub> unit is captured between two catalytically active metal ions (*e.g.* V<sup>2+</sup>). The structure is supposed to be formed by metal ion-hydroxide ion links in which the HO–Mg–OH bridge is of extreme importance.

## PLAN OF INVESTIGATION

The structure described above is obviously strongly dependent on pH. As it seemed important to be able to vary pH of the solution, we decided to try to substitute the metal ion-hydroxide ion structure with a more permanent one by using carbon-carbon bonds as building units.

The essential conditions for such a concept can be easily defined (*cf.* Fig. 1):

(1) It should contain two similar groups (X) both capable of binding low valent transition metal ions (M).

(2) The metal ions thus bonded should be situated at a certain distance from each other, optimal for the formation of the binuclear  $X-M-N \equiv N-M-X$  complex. This optimum distance should preferably correspond to the most frequent conformation of the structure.

(3) The structure should be rather rigid in its main part thus making it impossible for any conformation the molecule might take to establish a one-metal chelate  $-X-M-X-$ .

(4) On the other hand the structure must not be too rigid so that the release of the product ( $N_2H_4$ ) is excluded.

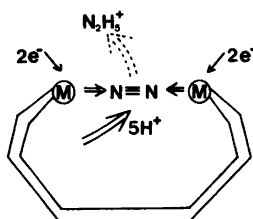


Fig. 1. Schematic description of a complex arrangement for the activation and reduction of the dinitrogen molecule to hydrazine.

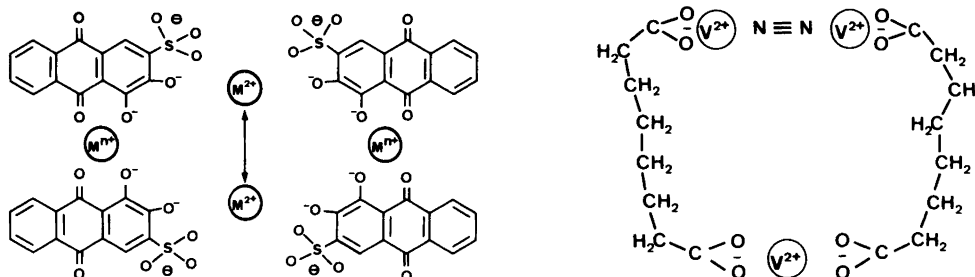


Fig. 2. (a) Cyclic structure of alizarin red S with different kinds of metal ions  $M^{n+}$  and  $M^{2+}$ ; (b) Crablike structure of a 3:2 complex of  $V^{2+}$  and 1,8-octanedioic acid.

From these starting-points we tried to synthesize a crablike molecule like that in Fig. 1 exclusively from organic building molecules.

This turned out to be quite difficult, however. We have chosen to try to knit together smaller pieces of organic material *via* one or several atoms of structure creating metal ions. This approach is then similar to Shilov's.

Some of the substances tested and the structures supposed to appear from them in aqueous solution are presented in Fig. 2.

The alizarine dye stuff can probably be compared to the catechol used successfully by Shilov and coworkers<sup>12-13</sup> to effect the reduction of  $N_2$  to  $NH_3$ . It has in fact been suggested<sup>14</sup> that polynuclear systems of the kind shown in Fig. 2a exist in solution.

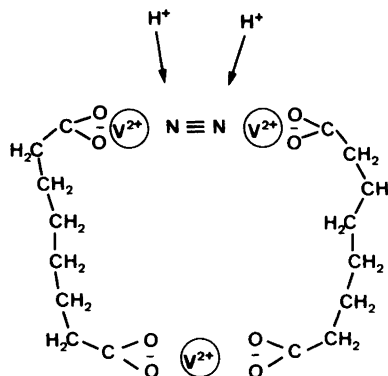
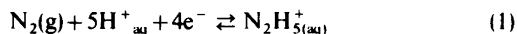
When the present work had been presented – at first as an internal report<sup>15</sup> – the extremely interesting work of Lehn<sup>16</sup> was brought to our attention.

The multi ring system of crown-ether-like units seems to offer great possibilities for the synthesis of exactly those semi-rigid ligands that we are discussing here.

## THERMODYNAMIC RELATIONS

The energy requirements for nitrogen fixation have been discussed in some detail by Shilov.<sup>7</sup> We recall here the thermodynamics of the formation of hydrazine.

The basic relation is



and the corresponding redox potential is

$$E = E_0 + \frac{RT}{4F} \ln \frac{P_{N_2} [H^+]^5}{[N_2H_5^+]} \quad (2)$$

Latimer<sup>17</sup> gives a value of  $E_0$  as  $-0,23$  V. Accepting this, one can represent the concentration of hydrazine in equilibrium with nitrogen at pressure  $P_{N_2}$  as a function of the redox potential  $E$  of the solution.

For  $T = 298$  K we get

$$\log [N_2H_5^+] = \log P_{N_2} - 5 \text{pH} + \frac{4}{0,058} (-0,23 - E) \quad (3)$$

This relation is represented graphically in Fig. 3 for some values of pH. It is evident from eqn. (3) that a low value of  $E$  and a low value of pH will give the highest possible value of the hydrazinium ion concentration. It is also evident that this concentration will be appreciable in aqueous systems only at rather extreme conditions.

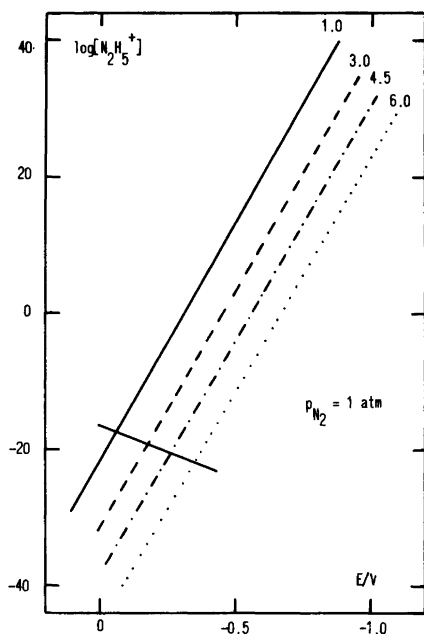


Fig. 3. The concentration of hydrazine as a function of the potential in the solution at various pH values (pH = 1, —); (pH = 3.0, - - -); (pH = 4.5, - . -); (pH = 6.0, ...). The line crossing the four parallel lines shows the situation if hydrogen at atmospheric pressure is in equilibrium with the solution.

The line crossing the four main lines of Fig. 3 will represent the concentration of  $N_2H_5^+$  in equilibrium with molecular hydrogen and molecular nitrogen, each of atmospheric pressure. It follows that the yield of  $N_2H_4$  from a reduction of  $N_2$  with  $H_2$  will be extremely small. It further follows that if the reduction potential  $E$  of the solution is to be maintained electrochemically, the hydrogen overpotential on the electrode must be considerable in order to avoid hydrogen liberation. (This situation might arise if one chooses to reduce the catalytically active metal ions electrochemically).

### PROCEDURE

The main part of the experiments have been carried out with vanadium(II) complexes as the  $N_2$ -binding/reducing system. The normal potential of the V(III)/V(II) couple is  $-0.25$  V (acid solution, Latimer<sup>17</sup>) and this might be expected to fit the requirements for interaction with the  $N_2/N_2H_4$  system ( $E_0 = -0,23$  V) rather well.

Some experiments have also been performed with chromium(II) as the reducing agent. The Cr(III)/Cr(II) system has a normal potential even lower than those mentioned above, but no hydrazine has been observed in these experiments. This may be related to the general sluggishness of Cr(III) complexes, making the liberation of reduced nitrogenous compounds difficult.

The main line of planning has been as follows:

(a) Selection of suitable ligand systems. In this phase the alizarine dye stuffs, phosphates of triaryl-methane derivatives as well as dicarboxylates, were tested.

(b) Optimisation of the ligand. As it was found that the dicarboxylates gave the most reproducible results, they were selected for further work.

Thus we studied the dependence of the yield on  $n$  in the series of  $^-OOC-(CH_2)_n-COO^-$  ( $3 \leq n \leq 10$ ).

(c) Factors of importance for increasing the yield were studied. First of all the electrochemical reduction of the V(III) species that were formed in the reaction.

The effects of additives were also investigated. The main reason for expecting any change in the yield was that the additives could possibly change the relative position of the redox potentials of the interacting systems.

(d) Starting from the results of point (b) the use of polymeric carboxylate systems were studied. The main idea was that the statistical distribution of

carboxylate units in a carboxyl containing copolymer should make possible the attainment of structures like the one in Fig. 1.

## EXPERIMENTAL

When not stated otherwise the chemicals were commercial products of *p.a.* quality and used without further purification. Vanadium(II) solutions were prepared by electrochemical reduction of vanadyl sulfate in dilute sulfuric acid according to a method by Herzog.<sup>18</sup>

It was found, however, that it was not possible to use commercial preparations of  $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$  as these contained occasional traces of nitrogenous substances yielding positive response for hydrazine on analysis. Therefore the vanadium(IV) sulfate was produced by treating  $\text{V}_2\text{O}_5$  in  $\text{H}_2\text{SO}_4$ -solution with ethanol as described in the literature.<sup>19</sup>

The experiments were performed in a glass flask containing the ligand solution. Nitrogen was bubbled through the solution at least one hour before adding the reducing agent (V(II)), then the solution was adjusted to the desired pH by adding aliquots of NaOH solution.

At suitable time intervals tests were then performed on hydrazine. A small volume of the solution was made alkaline and a solution of benzaldehyde in light petroleum (b.p. 71 °C) was added. Hydrazine reacts with the aldehyde to form an azine which is extracted into the organic phase. After separation of the organic phase it was treated with a dilute aqueous solution of hydrochloric acid containing *p*-dimethylaminobenzaldehyde. Then a new azine was formed, the yellow colour of which was determined spectrophotometrically.<sup>20</sup> A recording spectrophotometer (Hitachi EPS-3T) was used for this purpose. The absorbance was read at the maximum of the appropriate absorption band (458 nm).

A calibration curve was established from solutions of known hydrazine concentration. In all cases where a positive result was found blank tests were also made, using argon instead of nitrogen. Both gases were freed from oxygen by passing them through a solution of alkaline hydroquinone before they were led into the reaction flask.

In the experiments aimed at achieving an electrochemical reduction of vanadium(III) various working electrodes have been tried, *e.g.* active carbon-teflon electrodes with addition of polymers of cobalt ion phthalocyanine,<sup>21</sup> lead metal and stainless steel. The electrodes were formed as a round plate with a diameter of about 3 cm and fitted in a plexiglass frame. A saturated calomel electrode was used as reference electrode and a platinum foil as a secondary electrode. A potentiostat of type TR

40/3A was used to regulate the potential between the working electrode and the reference electrode.

Polymeric systems were prepared by copolymerizing styrene with acrylic acid and styrene with cinnamic acid. In both cases benzoylperoxide was used as an initiator. (The use of  $\alpha$ -azo-isobutyronitrile was abandoned because hydrazine was formed from residues of this reagent left in the polymer). The polymers were only sparingly soluble in water (pH=4.5) and in most cases the experiments were performed with a milky suspension to which the V(II) solution was added. The polymers of styrene/cinnamic acid were dissolved in tetrahydrofuran (THF). The THF-solution was then poured into water to give the milk-white suspension. The composition of the polymers were deduced from elemental analysis. The styrene/acid ratio was found to be lower than expected from the proportions of the ingredients.

## RESULTS

1. *Alizarine dyestuffs.* Of the various dye stuffs that were tested, only Alizarine Red S gave positive results. The best results were obtained in an aqueous solution of pH  $\approx$  4 and using  $\text{Mg}^{2+}$  or  $\text{Zn}^{2+}$  ions (as structure creating, *cf.* Fig. 2a) and  $\text{V}^{2+}$  ions as reducing units. The proportion of metal ions was  $\text{Mg}/\text{V} = 5:2$ .

The yield was about 50  $\mu\text{g}$  hydrazine, which corresponds to 0.3 % calculated on the amount of reducing agent. It is interesting to note that vanadium(II) ions only were not sufficient to get a reaction: The presence of a structure creating  $\text{Zn}^{2+}$  or  $\text{Mg}^{2+}$  unit was necessary.

2.  *$\alpha,\omega$ -Dicarboxylic acids.* The anions of dicarboxylic acids of the type  $\text{HOOC}-(\text{CH}_2)_n-\text{COOH}$  have been used as structure creating ligands in aqueous solutions. With such ligands we hoped to achieve a certain concentration of the complexes shown in Fig. 2b.

Actually these systems proved to be effective for hydrazine synthesis. The results are given in Table 1 at pH=4.5. This value of pH was chosen as preliminary experiments showed the best yield at this acidity.

The maximum values of hydrazine concentration given in Table 1 were reached within the short time required for saturating the solution with nitrogen (about 10 minutes). The experiment was not constructed for kinetic studies, though.

In Fig. 4 we have plotted the concentration of hydrazine against the number of  $\text{CH}_2$  groups in the

Table 1. The results of the attempts to reduce dinitrogen to hydrazine by using dicarboxylic acids as ligands and  $V^{2+}$  ions as reducing agent.

Ligand	Amount $V^{2+}$ mmol	Yield of $N_2H_4$ $\mu g$	Yield of $N_2H_4$ %	$C_{N_2H_4}$ $\mu M$
$HOOC(CH_2)_3COOH$	26.3	$12 \pm 3$	0.0057	1.17
$HOOC(CH_2)_4COOH$	20.6	$14 \pm 3$	0.0085	1.50
$HOOC(CH_2)_5COOH$	18.7	$16 \pm 3$	0.0107	1.73
$HOOC(CH_2)_6COOH$	17.3	$16 \pm 3$	0.0116	1.78
$HOOC(CH_2)_7COOH$	15.8	$10 \pm 3$	0.0079	1.08
$HOOC(CH_2)_8COOH$	14.7	$6 \pm 2$	0.0051	0.65
$HOOC(CH_2)_{10}COOH$	12.9	0	0	0

$\alpha,\omega$ -dicarboxylate. The highest concentration of hydrazine was obtained for 1,8-octanedioic acid, which has 6  $CH_2$  groups. The best arrangement of the 3:2 complex of Fig. 2b is met by  $n = 5$  or 6 in the formula above.

3. *Effect of additives.* When the catalytic effect of the  $\alpha,\omega$ -dicarboxylates had been established we investigated the effect of additives. Methanol showed no appreciable effect. In Fig. 5 we show the influence of dimethyl sulfoxide (DMSO) on the yield of  $N_2H_4$ . One observes a twofold increase in the yield. The reason for this is somewhat obscure, but it may very well be a true medium effect. In principle this can affect different factors of importance for the reaction.

(a) The  $pK_a$  of the acids and the stability constants of the V(II)-dicarboxylate complexes.

(b) The normal potential of the V(III)/V(II) couple.

(c) The normal potential of the  $N_2/N_2H_4$  system. The points (a) and (b) are of course interrelated.

4. *Electrochemical reduction.* The best results when trying to improve the yield of  $N_2H_4$  by reducing the V(III) electrochemically were achieved with porous electrodes of active carbon on which polymeric Fe-phthalocyanines were deposited.<sup>21</sup> The effect was not very pronounced, however. In most cases the yield was about twice that of experiments without electrochemical reduction. The cur-

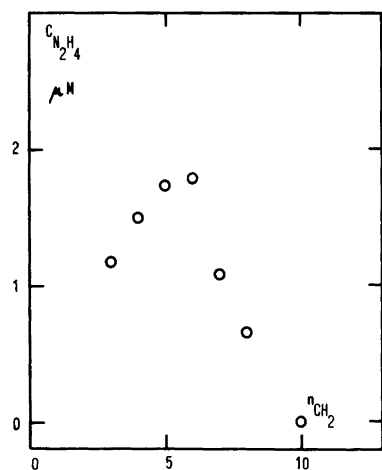


Fig. 4. The dependence of the hydrazine concentration on the number of  $CH_2$  groups in the  $\alpha,\omega$ -dicarboxylic acids, ( $n_{CH_2}$ ).

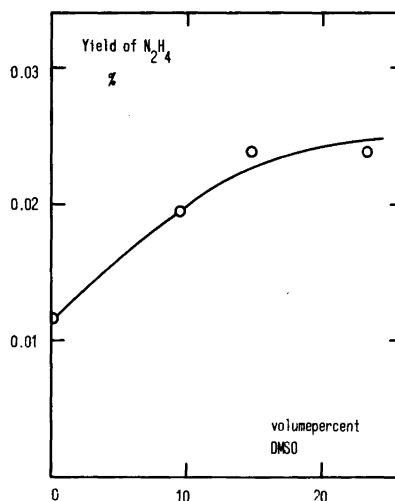


Fig. 5. The yield of hydrazine calculated on the amount of V(II) (17.3 mmol) as a function of the volume percent DMSO in the solutions.

rent efficiency was only about 1 %, indicating that most of the current was used to produce hydrogen. In order to improve the transport of oxidized species to the electrode we attempted to use some auxiliary redox systems, "mediators". These were methyl viologene ( $E^\circ = -0,44$  V), 2,2'-dipyridyl-1,1'-ethylene dibromide ( $E^\circ = -0,35$  V) and 2,2'-dipyridyl-1,1'-propylene dibromide ( $E^\circ = -0,55$  V). These substances are known to show high limiting currents at an electrode surface.<sup>22</sup> Thus if the reaction with vanadium(III) proceeded rapidly, one would have an efficient way of reducing the vanadium(III) electrochemically directly under conditions of the nitrogen fixation. However, we found that the amount of hydrazine formed when using the auxiliary redox systems did not noticeably exceed the amount formed without it. There may be three reasons for this: Either the reaction between V(III) and the reduced form of the mediator did not proceed fast enough at the experimental conditions. Or the platinum foil used to sense the redox potential of the solution brought about a catalytic decomposition of hydrazine. Or possibly there was an increase of the efficiency of the reduction of hydrogen at the electrode. This would decrease the concentration of the reduced form of the mediator near the electrode and thus decrease diffusion into the solution. The redox potential of the solutions was found to be only  $-0,1$  to about  $-0,2$  V (relative to NHE). This is a surprisingly high potential and one must remember the possibility of catalytic processes on the electrode giving false potentials. Another even more serious possibility is that oxygen or hydrogen peroxide diffuses from the anode compartment through the glass frit that separates the anode and cathode compartments.

5. *Polymeric carboxylates.* Although the systems described up to now are by no means homogeneous, they are nevertheless of low-molecular origin.

If the catalytic synthesis could be run with polymeric polycarboxylates, preferably hydrophobic and insoluble, easier processing of the reaction would be possible.

Therefore one series of cinnamic acid-styrene and one series of acrylic acid-styrene copolymers were prepared and the yield of hydrazine measured as a function of the styrene/carboxylic acid ratio. Statistically one expects a distribution of the carboxylate groups that is a function of this ratio.

One could then find arrangements such as those depicted in Fig. 6. Depending on the orientation of

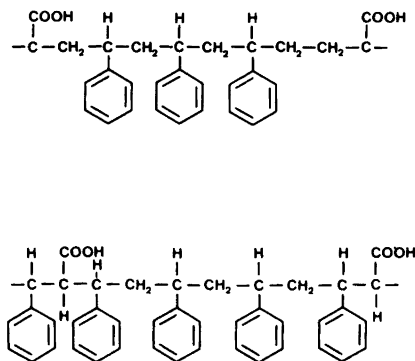


Fig. 6. Possible arrangements of the monomeric groups in the copolymers used for catalysis. Upper formula styrene/acrylic acid of composition 3:1. Lower formula styrene/cinnamic acid of composition 3:1.

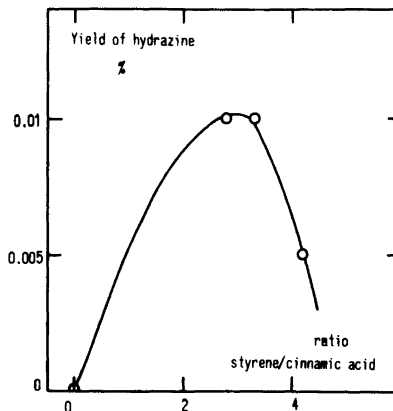


Fig. 7. The yield of hydrazine calculated on the amount of added V(II) (5 mmol) as a function of the ratio styrene/cinnamic acid in the polymers.

the components a 3:1 sequence would yield 8–10 carbon groups separating the carboxylates and a 2:1 sequence would yield 6–10 such groups. For the styrene/acrylic acid system the highest yield of hydrazine was found when the ratio of these components was 3:1.

The results for the styrene/cinnamic acid system are shown in Fig. 7. Also in this case a maximum of the yield seems to appear at a reagent ratio of about 3:1.

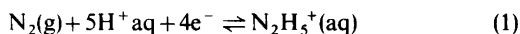
It is interesting to observe that the yield of hydrazine is very similar to that found for the

simple  $\alpha,\omega$ -dicarboxylate systems. Indeed, as the COO---COO separation is probably closer to 8 CH<sub>2</sub> groups than to 6 (the number found more efficient for the dicarboxylate, *cf.* Fig. 4) it is astonishing that the yield is as high as observed. Perhaps the many phenyl groups favour a certain conformation of the polymer chain, giving an effective distance between the carboxylate groups close to that of the simpler systems. Alternatively, the hydrophobic environment can cause effects like those found when adding DMSO.

## DISCUSSION

The far most important questions facing us are: Has catalysis been achieved? Are the concentrations of hydrazine detected those that can be expected under the experimental conditions if equilibrium is established (*i.e.* if the reactions proceed rapidly by a catalytic process)?

To answer these questions, let us consider the reactions



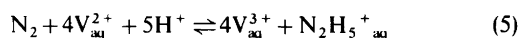
$$E^\circ = -0.23 \text{ V}$$

and



$$E^\circ = -0.25 \text{ V}$$

From the addition of these two reactions we get



with

$$\Delta G^\circ = -4F(0.25 - 0.23) \quad (6)$$

$$\text{As } RT \ln K = -\Delta G^\circ \quad (7)$$

where  $K$  is the equilibrium constant of reaction (5)

$$K = \frac{[\text{V}_{\text{aq}}^{3+}]^4 [\text{N}_2\text{H}_5^+]}{P_{\text{N}_2} [\text{V}_{\text{aq}}^{2+}]^4 [\text{H}^+]^5} \quad (8a)$$

it holds for  $T = 298 \text{ K}$  that

$$\log K = \frac{4(0.25 - 0.23)}{0.058} = 1.4$$

$$K = 25 \text{ M}^{-4} \text{ atm}^{-1} \quad (8b)$$

It is now possible to calculate the equilibrium value of  $[\text{N}_2\text{H}_5^+]$  for any value of pH, given that we know the concentrations  $[\text{V}_{\text{aq}}^{2+}]$  and  $[\text{V}_{\text{aq}}^{3+}]$ .

For the sake of discussion, let us assume that  $[\text{V}_{\text{aq}}^{2+}] = C_{\text{V(II)}}$  and  $[\text{V}_{\text{aq}}^{3+}] = C_{\text{V(III)}}$ , where  $C_{\text{V(II)}}$  indicates the total concentration of the species in question. Let us further assume that the three-valent vanadium is formed solely from reaction (5). This means that no other oxidation of V(II) has taken place.

Thus it holds that

$$[\text{V}_{\text{aq}}^{3+}] = 4[\text{N}_2\text{H}_5^+] \quad (9)$$

Now, considering the case of 1,8-octanedioic acid (Table 1), one gets

$$C_{\text{V(II)}} = \frac{17.3}{0.28} = 62 \text{ mM} \quad (10)$$

and

$$\text{pH} = 4.5 \quad (11)$$

$$P_{\text{N}_2} = 1 \text{ atm} \quad (12)$$

Introducing eqns. (9)–(12) into eqns. (8a) and (8b) one gets

$$\frac{(4[\text{N}_2\text{H}_5^+])^4 [\text{N}_2\text{H}_5^+]}{1 \times (62 \times 10^{-3})^4 (10^{-4.5})^5} = 25 \quad (13)$$

Solving eqn. (13) for  $[\text{N}_2\text{H}_5^+]$  gives

$$[\text{N}_2\text{H}_5^+] = 2.1 \times 10^{-6} \text{ M} \quad (14)$$

This value agrees very well with the one found experimentally  $(1.8 \pm 0.3) \times 10^{-6} \text{ M}$ . To the best of our understanding this result shows that the reaction (5) is proceeding with an appreciable speed to reach a state of equilibrium during the time of the experiment. The reaction (5) does not in itself proceed with a measurable rate at the pH and temperature used. It is thus catalyzed by the  $\alpha,\omega$ -dicarboxylate ions that are present in the system. Referring to Fig. 4 it is obvious that this

catalytic effect is most pronounced if the number of the  $\text{CH}_2$  groups is  $n = 5$  or 6.

We can now answer the questions put forward above: The reduction of dinitrogen by vanadium(II), *i.e.* reaction (5) is effectively catalyzed by some  $\alpha,\omega$ -dicarboxylate ions in the sense that the reaction (5) reaches an equilibrium state. The general reduction of dinitrogen, *i.e.* reaction (1), is not catalyzed unless the vanadium(III) is continuously reduced. The yield of hydrazine, can be increased – in principle – by removing the vanadium(III), *e.g.* by a selective extraction, but not more than a stoichiometric reaction can be hoped for unless V(III) is reduced. Our calculation above must be looked upon with a certain reservation, though. One reason for this is that the value of  $C_{\text{V(III)}}$  is obviously of the order of magnitude  $8 \times 10^{-6}$  M. This means that even a small amount of oxygen which cannot be avoided in the system will cause a rather appreciable change of the  $C_{\text{V(III)}}/C_{\text{V(II)}}$  ratio, *i.e.* increasing the redox potential of reaction (4) towards less negative values. This effect would result in a decrease of the hydrazine equilibrium concentration.

Another reason for concern is that the vanadium species of the system is not all the  $\text{V}_{\text{aq}}^{2+}$  of eqns. (4) and (5), but rather some carboxylate complex. This reflects, of course, the very idea of the catalytic arrangement.

The ratio  $(\text{V}_{\text{aq}}^{3+})/(\text{V}_{\text{aq}}^{2+})$ , of importance in applying eqns. (8), can be estimated if the degree of complexation were known. Limiting the argument to the case of only the 1:1 complex (as the metal to ligand ratio is  $> 1$ ) one can write

$$\frac{[\text{V}_{\text{aq}}^{3+}]}{[\text{V}_{\text{aq}}^{2+}]} = \frac{C_{\text{V(III)}}}{C_{\text{V(II)}}} \cdot \frac{1 + \beta_1^{\text{II}} \cdot [\text{L}]}{1 + \beta_1^{\text{III}} \cdot [\text{L}]} \quad (15)$$

In this expression we use the conventions of solution chemistry,

$$\beta_1^{\text{II}} = \frac{[\text{ML}]}{[\text{M}][\text{L}]} \text{ for V(II)}$$

$$\beta_1^{\text{III}} = \frac{[\text{ML}]}{[\text{M}][\text{L}]} \text{ for V(III)}$$

where  $[\text{L}]$  is the free ligand concentration.

The ligand being in this case a bidentate, probably not chelating, ion, in this context it would be preferable to treat L as one half of that ion. This means that it should be rather close in properties to the acetate ion.

Unfortunately no determination of the acetate complexity of V(II) and V(III) seems to have been made, Ref. 23. Indeed, from the collection of stability constants by Sillén and Martell,<sup>23</sup> very few investigations on both V(III) and V(II) systems are reported. In Table 2 we have put together some of the available<sup>23</sup> data, both for V(III)/V(II) systems and for Fe(III)/Fe(II) systems, the latter because of their greater abundance.

It appears that  $\log \beta_1^{\text{III}} - \log \beta_1^{\text{II}}$  for vanadium and a univalent "hard" ligand<sup>24</sup> should be about 1.8 and a reasonable estimate of  $\log \beta_1^{\text{III}}$  and  $\log \beta_1^{\text{II}}$  should be about 3.4 and 1.6.

Now we can introduce these estimates into eqn. (15) by using for  $[\text{L}]$  the value that arises from a treatment of the V(II) system alone.

$C_{\text{L}} = \frac{2}{3} C_{\text{V(III)}} = 42$  mM from Table 1 and for the same system that was treated above.

$[\text{L}]$  emerges as 17 mM from a combination of the equations

Table 2. Model systems for estimating  $\beta_1^{\text{II}}$  and  $\beta_1^{\text{III}}$  for the vanadium–carboxylate complexes.

	EDTA			Acetate			SCN		Assumed values for the vanadium carboxylate constants
	$\log k_1$	$\frac{1}{6} \log k_1$	Ref.	$\log \beta_3$	$\log k_1$ $\frac{1}{3} \log \beta_3$	Ref.	$\log k_1$	Ref.	
V(II)	12.70	2.1	25				1.04	30	1.6
V(III)	25.9	4.3	25				2.18	30	3.4
Difference		2.2					1.1		
Fe(II)	14.3	2.4	26		1.40	27	0.85	31	
					1.82	28			
Fe(III)	25.1	4.2	26		3.2; 3.4	29	2.19	32	
Difference		1.8		10.32	3.4	28			
					1.8		1.3		



$$\bar{n} = \frac{\beta_1[L]}{1 + \beta_1[L]} \quad (16a)$$

and

$$\bar{n} = \frac{C_L - [L]}{C_M} \quad (16b)$$

This gives us from eqn. (15) the relation

$$\frac{[V_{aq}^{3+}]}{[V_{aq}^{2+}]} = \frac{C_{V(III)}}{C_{V(II)}} \cdot \frac{1 + 40 \times 17 \times 10^{-3}}{1 + 2500 \times 17 \times 10^{-3}} = \frac{C_{V(III)}}{C_{V(II)}} \frac{1}{26}$$

which means that the redox potential of the vanadium(II) solution is really 0.08 V lower than for an acidic vanadium solution. This means that the "conditional equilibrium constant" should be considerably larger than the value used in the calculations above, giving a higher value of the hydrazine concentration. However, as stated before, the unavoidable presence of small quantities of V(III) not originating from reaction (5) will tend to give smaller values of the hydrazine concentration. These effects may more or less cancel each other. Furthermore, one must remember that at pH=4.5 a part of the carboxylate is protonized. Hence the total carboxylate concentration is really only a fraction of what has been used in the calculation of  $(V^{3+})/(V^{2+})$  giving a somewhat smaller reduction factor of this quantity.

Also, the calculations are admittedly very approximate and no account has been taken of the fact that at least some part of the vanadium complexes appears as solid precipitates. Another effect that has been neglected is the possibility of hydrazine-vanadium complexes.

All these considerations show that the figure of  $[N_2H_5^+]$  calculated from eqn. (13) should be looked upon with some reservation. The order of magnitude is the right one, however. The points discussed above do not diminish the value of the general conclusion: The dicarboxylate ions catalyze the reaction between V(II) and  $N_2$ .

## DISCUSSION OF SIMILAR INVESTIGATIONS

It must be noted that the conclusions similar to those just presented have been put forward also by Shilov and his coworkers. Indeed — as pointed out in the beginning of this paper — the work by

Shilov *et al.* was the inspiration for this investigation. It might seem contradictory, at first, that one gets a better yield with Shilov's method, using strongly alkaline solutions. It follows from Fig. 3 that for a given reduction potential imposed on the solution a low pH implies a large yield and *vice versa*. The fact that a good yield is found for the alkaline (Mg, V) system<sup>11</sup> must originate from a drastic reduction of the redox potential of the V(II)/V(III)-couple in an alkaline medium. This is actually the case.<sup>17</sup>

However, this effect introduces a difficulty in reducing the V(III) after the reaction as the decrease in redox potential is obviously caused by  $V(OH)_3$  being much more insoluble than  $V(OH)_2$ . Expressed in another way, the hydroxo complexes of V(III) are much stronger than those of V(II). This means that the free concentration of vanadium(III), *i.e.*  $[V^{3+}]$ , is extremely low.

Electrolytic reduction must therefore be difficult unless the hydroxo complexes have a concentration high enough to permit reduction at an electrode.

Indeed it seems that in order to perform a reduction, alternating shifts between alkaline and acidic conditions are necessary. In this way, it was possible to perform a reduction of  $N_2$  to hydrazine by molecular hydrogen.<sup>7,33</sup>

Whereas our system was heterogeneous (or possibly both homogeneous and heterogeneous) like the (Mg,V)  $(OH)_2$  system described by Shilov,<sup>11</sup> some truly homogeneous systems have also been reported.<sup>12,13,34</sup> They contain V(II) complexes of catechol and other polyhydroxo phenols.

By a kinetic treatment<sup>34</sup> the authors arrive at the conclusion that a polynuclear complex is necessary for the reaction. It is pointed out<sup>13</sup> that probably 4 vanadium(II) atoms are required at these pH-values (8–9) to supply the necessary numbers of electrons for the reduction of  $N_2$  to  $N_2H_4$ . The main model is very similar to that suggested here.

To sum up the present observations on V(II) systems for reduction of  $N_2$ : The reaction is not catalytic but yields V(III) as a product. The larger the difference between the redox potential of the V(II)/V(III) couple and the redox potential of the  $N_2/N_2H_4$  couple, the larger the yield will be. A very negative redox potential of V(II)/V(III) obviously increases the possibility of hydrogen evolution, however, thus reducing the gain.

The maximum of efficiency found with our dicarboxylate systems at about pH=4.5 is then easily explained: For lower pH values the carboxylate

groups are protonized, hindering the formation of complexes. For higher pH values the concentration of the carboxylates does increase but only to a maximum value given by the actual total concentration. Hence the redox potential of the V(II)/V(III) system does not change appreciably. The redox potential of the  $N_2/N_2H_4$  system follows eqn. (5), resulting in a gradually less favourable yield with rising pH.

### Properties of the ligands

The observations made (Fig. 4), that the number of  $CH_2$  groups in the  $\alpha,\omega$ -dicarboxylates determine the amount of hydrazine produced, seem to strengthen our general scheme: For a certain geometrical arrangement the coordination of  $N_2$  between the two metal atoms is facilitated and the reaction proceeds rapidly. This reasoning could hold also for the Mg–V–OH gels of Shilov's work as well as for the polymeric carboxylates studied in this investigation (Figs. 6 and 7).

Another possible explanation could be that all the dicarboxylates are equally effective *per se*, but that the  $pK_a$  and the stability constants of the V(II) and V(III) complexes are changing in a systematic way with  $n_{CH_2}$ , so as to produce a less negative redox potential for  $n < 4$  and  $n > 7$ .

This is, however, not very likely as such systems should have a tendency to form chelates, which will probably be *more* stable for V(III) than for V(II) and consequently give *more* negative redox potentials. Furthermore, if chelates were formed to a great extent the possibility of achieving the arrangement of Fig. 2b would be decreased.

Thus we still prefer our first theory, that of an optimal geometric arrangement. As mentioned before, this view is supported by the fact that optimum efficiency seems to appear at about the same number of intervening  $CH_2$  groups in the polymeric polycarboxylates as in the low-molecular dicarboxylate complexes.

*The electroreduction.* Some of the problems have been discussed already when the experimental results were presented. It should be reemphasized here, though, that a suitable auxiliary redox system must be looked for to improve the reducing efficiency of an electrode. This system should have such properties that it willingly reacts with the vanadium(III) that is probably bound to a dicarboxylate precipitate of some kind or possibly

strongly bound in a soluble complex. (Anyway the concentration of free  $V_{aq}^{3+}$  is small).

The auxiliary redox system must also have a low molecular weight so that it diffuses rapidly to and from the site of reaction and to and from the electrode surface.

The polarization of the electrode necessary to make the reaction go, must be as small as possible to avoid the unwanted production of hydrogen or even worse, of metallic vanadium.

It is obvious that further research is needed to test the suggested explanations for the malfunctioning of the system.

### CONCLUSIONS

Two main points emerge from this study:

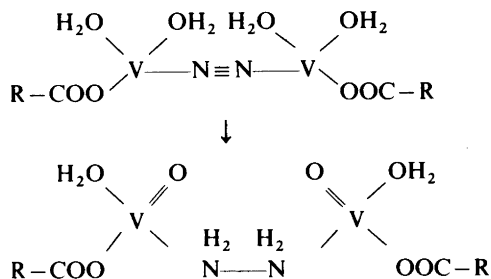
(a) The reduction of dinitrogen to hydrazine by vanadium(II) is effectively catalyzed by  $\alpha,\omega$ -dicarboxylates or polymeric polycarboxylates, given that the distance between the carboxylate groups is of suitable size.

(b) The study of the electrochemistry of vanadium(III) is of vital importance for continued progress in this field.

Moreover, some ideas for future work may be outlined: It is obvious that a decrease of pH will increase the yield for a given redox potential of the solution. Hence, if a ligand can be found that coordinates not too weakly to vanadium(II) ions but at the same time has a low proton affinity one would have the ideal system for nitrogen fixation. Such ligands will most probably be some kind of multi-ring crown-ethers as suggested by Lehn.<sup>16</sup> The model proposed here is, indeed, an example of the "cascade complexing":<sup>16</sup> the dicarboxylate first coordinates the vanadium ions and this new system thereafter coordinates the dinitrogen molecule.

The obvious difficulty in reducing the dinitrogen molecule to hydrazine or even further to ammonia is that a transfer of 4 or 6 electrons must take place. Shilov<sup>7</sup> points out that the appearance of  $N_2H_2$  as a reaction intermediate should require a reducing power of the catalyst so that water would be decomposed. Therefore it seems that there must be a transfer of four electrons and four protons, more or less at the same time. This situation may arise with metal ions of suitable properties. It seems to us that the vanadium system offers these properties.

Hence one can imagine as the reaction mechanism the "simultaneous" transfer of four hydrogen atoms



The oxovanadium(IV) thus formed is rapidly reduced by excess vanadium(II) ions. The process described above is obviously facilitated by the attraction of the positively charged H atoms on the water molecule by the negatively charged  $\text{N} \equiv \text{N}$  group.

The transfer of charge in an  $\text{M}-\text{N} \equiv \text{N}$  bond is such that the nitrogen atoms are negatively charged. This has been shown experimentally by us<sup>35</sup> and others<sup>36</sup> as well as from theoretical calculations.<sup>37,38</sup>

A complete reduction of  $\text{N}_2$  to  $\text{NH}_3$  must, however, proceed by stages as is done also in the enzymatic reduction.<sup>8</sup> Thus the aim is to find a catalytic system that reduces  $\text{N}_2\text{H}_4$  further to  $\text{NH}_3$  or incorporates it into a carbon-nitrogen bond.

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