Mechanism of the reduction of molecular nitrogen to hydrazine by niobium(III) hydroxide

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The effect of the concentration of water on the rate of reduction of molecular nitrogen to hydrazine by niobium(III) hydroxide in alkaline H_2O—MeOH and D_2O—MeOD mixtures was studied. In both cases, the reaction rate is maximum when $[H_2O] = 4$ mol L^{-1}, and the inverse isotopic effect ($k^D/k^H > 1$) is observed when $[H_2O] < 20$ mol L^{-1}. Similar regularity was observed for the reaction of hydrogen elimination. It was found that HD is formed in the H_2O—MeOH system in the presence of D_2. The conclusion was made that the rate-determining stage in hydrazine formation is the transfer of a hydride ion to the dinitrogen molecule coordinated to the binuclear Nb^{III} center. A kinetic scheme satisfactorily explaining the effect of the concentration of water ($[H_2O] = 1.5$—49.0 mol L^{-1}) on the reaction rate constant was proposed.

Key words: molecular nitrogen, reduction; hydrazine; hydroxide ion; hydride ion; reverse isotopic effect.

Reduction of molecular nitrogen to hydrazine by transition metal hydroxides occurs efficiently only in alkaline water-methanol media. It has been established that metal hydroxopolymers formed at the initial stage[1] react in reversible reactions with molecules of N_2, solvent, and bases (OH^-, MeO^-). Molecules of H_2O in the coordination sphere of the hydroxopolymer are deprotonated by a base; as the result, the polynuclear hydroxo complex gains a negative charge, which increases as the concentration of alkali increases.[2] Methanol must be necessarily present in the reaction mixture because it is capable of forming a stronger base, the MeO^- ion, under the action of alkali. This ion deprotonates water molecules more efficiently than OH^-. In the presence of MeOH, the formation of hydrazine is observed at lower pH.[3,4] An increase in the negative charge gives the hydroxo cluster reductive properties and is necessary for the synthesis of N_2H_4, which occurs only in strongly alkaline media ($E_0 = -0.36$ V).[5] In addition, an increase in the negative charge of the aquahydroxo cluster favors the appearance of hydride forms of the cluster, which play the role of active centers in the formation of hydrazine and H_2.[6]

A study of the kinetics of the reduction of N_2 to hydrazine in protic (H_2O—MeOH) and deuterated (D_2O—MeOD) solvents in Mo-containing hydroxide systems[7] has established that an inverse isotopic effect ($k^D/k^H > 1$) is observed under conditions optimum for the formation of N_2H_4. This was explained in terms of a two-stage mechanism of the reaction including the equilibrium formation of a hydride metal complex followed by the transfer of the H^- ion to the N_2 molecule in the coordination sphere of a binuclear fragment of the polymeric hydroxide.[8] This mechanism has been directly confirmed by the isotope exchange of D_2 with a protic solvent.

It is of interest to compare catalytic systems containing different transition metals. For example, the d^4-electron configuration of Cr^{II} rules out the possibility of the formation of an active center based on one hydroxide chain,[9] and the d^1-electron configuration of Ti^{III} is the reason for the inertness of the hydroxide of this metal toward dinitrogen.[10]

This work, continuing the study of the mechanism of the reduction of molecular nitrogen, studied the reduction of N_2 to hydrazine by the most active to dinitrogen Nb^{III} hydroxide with the d^2-electron configuration.

Experimental

Molecular nitrogen was reduced in a glass two-chamber vessel placed in an autoclave at 288 K according to a procedure described previously.[9,11,12] The initial niobium(III) compounds were obtained by the reduction of a hydrochloric solution of $NbCl_5$ in MeOH by a 2% zinc amalgam for 10 min. The content of Nb^{III} was determined by titration with ammonium vanadate in an atmosphere of Ar. The concentration of water in the reaction medium was varied from 1.2 to 50 mol L^{-1}, and the minimum amount of water was determined only by the reaction of KOH with MeOH. The concentration of alkali in the reaction medium was determined by a known procedure.[4] The quantity of alkali necessary for com-

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plete precipitation of $Nb(OH)_3$ was determined by pH-metry. The H/D exchange was carried out at 313 K in a Rittenberg vessel for 40 min (p_{D_2} = 0.83 · 10^5 Pa).[6] The degree of exchange was established by mass spectral analysis of the gaseous phase. Experiments on H_2 evolution were carried out in an atmosphere of Ar under the same conditions as the reduction of N_2. After the completion of the experiment, the reaction mixture was moved into a 6 *N* solution of H_2SO_4 saturated with argon and titrated by ammonium vanadate in an inert atmosphere in the presence of phenylanthranilic acid. The quantity of evolved hydrogen was determined from the amount of oxidized Nb^{III}.

Results and Discussion

When Mo-containing hydroxides[7] and $Cr(OH)_2$[9] are used, the rate of N_2 depends not only on the concentration of alkali but also on the H_2O/MeOH ratio. Our experiments performed in a wide range of water concentrations showed that the rate of formation of hydrazine during the reduction of N_2 by Nb^{III} hydroxide in a protium (H_2O—MeOH) medium and in a deuterated (D_2O—MeOD) medium passes through a maximum (Fig. 1), which is typical of nitrogen-fixation systems.[7,12] It can be seen in Fig. 1 that when $[H_2O] < 20$ mol L^{-1}, the reaction occurs at a higher rate in the deuterated solvent ($k^D/k^H > 1$), and when the concentration of water is higher, the rate is greater in the H_2O—MeOH mixture ($k^H/k^D > 1$) (Table 1).

In the reaction of H_2 evolution under the same conditions, the isotope effect changes similarly to the change in the k^D/k^H value when hydrazine is formed (see Table 1).

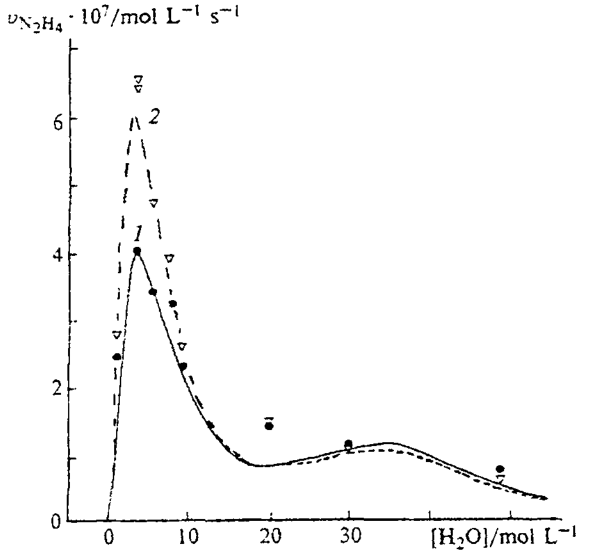


Fig. 1. Effect of the concentration of water on the rate of formation of hydrazine in the H_2O—MeOH (*1*) and D_2O—MeOD (*2*) systems. Curves indicate calculation, points indicate experiment; $[Nb^{3+}] = 4 \cdot 10^{-2}$ mol L^{-1}, [KOH] = 1 mol L^{-1}, p_{N_2} = 8.1 MPa, T = 288 K.

Table 1. Effect of the concentration of water on the isotopic effect in the formation of hydrazine and dihydrogen

$[H_2O]$ /mol L^{-1}	H_2O/MeOH*	k^D/k^H	
		N_2H_4	H_2
1.5	0.062	1.10	1.15
4.0	0.170	1.63	1.19
6.0	0.265	1.37	—
8.0	0.370	1.20	—
9.5	0.452	1.06	—
20	1.260	0.98	—
30	2.620	0.87	0.78
48.8	15.400	0.89	—

* Molar ratio.

The MS analysis in the gaseous phase after the experiment in an atmosphere of D_2 showed the presence of HD in a concentration of 1.3±0.02 mol.%. This is significantly greater than the value of exchange in the presence of $Cr(OH)_2$ and correlates with the nitrogen-fixation activity of these hydroxides.[9]

In previous works, the effect of the water content on the reaction rate of dinitrogen reduction[8,9] has been studied in a fairly narrow range of H_2O concentrations, which made it possible to restrict the analysis of the experimental data to only those solvate equilibria in which the number of water molecules in the coordination sphere of metal complexes changes by unity only. In the case of the niobium system, the concentrations of water and methanol vary over a wide range, which makes it possible to take into account all equilibria determining the content of free water (*W*) and free alcohol (*C*) in the system:

$$(OR^-)_{solv} + H_2O \xrightleftharpoons{K_h} (OH^-)_{solv} + ROH,$$

$$H_2O + X^-(H_2O)_{p-1}(ROH)_{4-p} \xrightleftharpoons{K_s} X^-(H_2O)_p(ROH)_{3-p} + ROH \quad (p = 1 \text{ to } 3), \qquad (1)$$

$$H_2O + K^+(H_2O)_{x-1}(ROH)_{5-x} \xrightleftharpoons{K_s} K^+(H_2O)_x(ROH)_{4-x} + ROH \quad (x = 1 \text{ to } 4),$$

where X = OH^-, OR^-; R = Me.

According to the data of the analysis,[8] the number of strongly bound solvent molecules in the solvate shells of anions and cations is equal to 3 and 4, respectively. The value K_h = 144 was calculated from the experimental values of the autoprotolysis constants of water and methanol. It was assumed that this was independent of the isotopic composition of the solvent. Since the necessary data are lacking, this approximation was used in our previous works as well. This approximation corresponds to the assumption that the change in the ion products of water and methanol is the same after isotope substitution. Only one constant, K_s, is used for description of all equilibria, which simplifies the kinetic analysis and decreases considerably the number of unknown parameters. Let us introduce the following variables for a quantitative description of the solvate equilibria:* x is the overall concentration of OH^- ions,

$$x = x_1 + x_2 + x_3 + x_4;$$

y is the overall concentration of OR^- anions,

$$y = y_1 + y_2 + y_3 + y_4;$$

β is the overall concentration of KOH,

$$\beta = z_1 + z_2 + z_3 + z_4 + z_5,$$

where

$$x_i = [OH^-(H_2O)_{4-i}(ROH)_{i-1}],$$

$$y_i = [OR^-(H_2O)_{4-i}(ROH)_{i-1}],$$

$$z_i = [K^+(H_2O)_{5-i}(ROH)_{i-1}].$$

Then taking into account the following equations

$$x_k = \left[\frac{C}{K_sW}\right]^{k-1} \cdot \frac{\beta C}{C + K_hW} \cdot \frac{1 - C/(K_sW)}{1 - [C/(K_sW)]^4},$$

$$y_k = \left[\frac{C}{K_sW}\right]^{k-1} \cdot \frac{K_h\beta C}{C + K_hW} \cdot \frac{1 - C/(K_sW)}{1 - [C/(K_sW)]^4},$$

$$z_k = \left[\frac{C}{K_sW}\right]^{k-1} \cdot \beta \cdot \frac{1 - C/(K_sW)}{1 - [C/(K_sW)]^5}$$

the system of equations can be reduced to four equations for x, y, and for concentrations of free water and alcohol (W and C, respectively):

$$K_hxC = yW,$$

$$x + y = \beta,$$

$$x + W + 3x_1 + 2x_2 + x_3 + 3y_1 + 2y_2 + y_3 + 4z_1 + \\ + 3z_2 + 2z_3 + z_4 = W_0,$$

$$y + C + x_2 + 2x_3 + 3x_4 + y_2 + 2y_3 + 3y_4 + z_2 + \\ + 2z_3 + 3z_4 + 4z_5 = C_0,$$

where W_0 and C_0 are the overall concentrations of water and alcohol, respectively. Since the x and y values can be easily expressed through C and W, and the concentrations of free water and free alcohol are related by the correlation

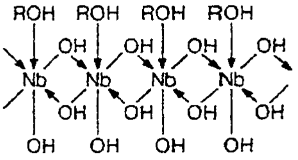
$$W + C + 8\beta = W_0 + C_0,$$

the following equation for calculation of W can be obtained:

$$W/\beta + (3 + 2a + a^2)/(1 + a + a^2 + a^3) + \\ + (4 + 3a + 2a^2 + a^3)/(1 + a + a^2 + a^3 + a^4) + \\ + 1/(1 + K_hK_sa) = W_0/\beta, \quad (2)$$

where $a = (C_0 + W_0 - W - 8\beta)/(K_sW)$. Since the concentration of niobium is very small, the solution of Eq. (2) also determines the content of free water in the $Nb(OH)_3$—alcohol—water system. A change in the concentration of water in the system affects in turn the ratio of the water to alcohol molecules in Nb^{III} hydroxopolymers, whose structure can be presented by Scheme 1.

Scheme 1



R = H, Me

Let us assume that all hydroxopolymers contain the same statistical mean number of units in the chain, equal to m. Then from the system of equations

$$Nb_m(OH)_{3m}(H_2O)_n(ROH)_{m-n} + H_2O \overset{K}{\rightleftharpoons} \\ \rightleftharpoons Nb_m(OH)_{3m}(H_2O)_{n+1}(ROH)_{m-n+1} + ROH$$

with account for

$$\sum_{n=0}^{m} M_n = [Nb],$$

Where $M_n = [M_m(OH)_{3m}(H_2O)_n(ROH)_{m-n}]$, we have

$$M_n = (\alpha^n - \alpha^{n-1})/(1 - \alpha^{m+1}) \cdot [Nb],$$

where $\alpha = KW/C$, assuming that the equilibrium constant of hydrolysis K is independent of the overall water content.

In the subsequent reactions of the hydroxo polymer with a base (all ligands except three water molecules are omitted),

$$[Nb_m(H_2O)_3] + 2\,(RO^-)_{solv} \overset{K_H}{\rightleftharpoons} \\ \rightleftharpoons [Nb_m(OH)_2H]^- + 2\,H_2O + (OH^-)_{solv} + 3\,Solv$$

(Solv = H_2O, MeOH)

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* We use the formal scheme for description of equilibria (1) based on concentrations rather than activities of components of the system. However, this scheme takes into account differences between ions with different compositions of solvate shells; therefore, the comparison of this system with the approximation of ideal solutions makes it possible to estimate true activity coefficients of water and alcohol.

an active hydride-containing complex is formed:

$$[Nb_m(OH)_2H]^- + N_2 \xrightarrow{k} \text{Products.}$$

It can be assumed that deprotonated water molecules are located at adjacent metal atoms in the hydroxide chain. Assuming even distribution of n water molecules along the chain and approximately evaluating the probability of the correlated arrangement of three water molecules, we obtain the final expression for the rate of formation of hydrazine from N_2 (Eq. (3))

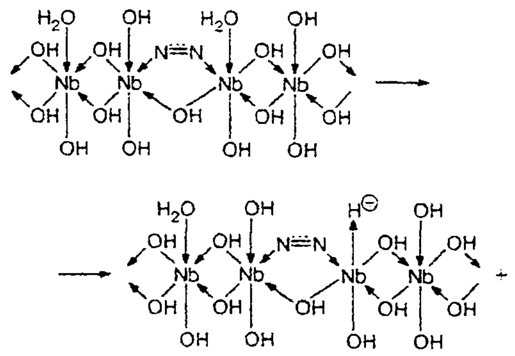
$$v = \frac{[Nb]\cdot[N_2]\cdot\beta}{W(C+K_{\mathrm{H}}W)}\cdot\frac{K_sW-C}{(K_sW)^4-C^4}\cdot K_{\mathrm{H}}k \times \\ \times\sum_n \frac{n(n-1)(n-2)\left[(KW/C)^n-(KW/C)^{n+1}\right]}{1-(KW/C)^{m+1}}, \qquad (3)$$

containing two nonlinear parameters and one linear parameter $u = [N_2]K_{\mathrm{H}}k$. The values $K = 0.357$, $K_s = 9.55$, and $u = 3.85\cdot10^{12}$ mol^4 L^{-4} s^{-1} for the protic medium and $K = 0.378$, $K_s = 12.09$, and $u = 6.23\cdot10^{12}$ mol^4 L^{-4} s^{-1} for the deuterated solvent were determined by the least-squares method.*

The obtained theoretical dependences of v were compared with the experimental dependences (see Fig. 1). The maximum divergence observed in the region of $[H_2O] = 20$ mol L^{-1} is not substantial because it is caused by approximations accepted for describing the system with the purpose of decreasing the number of parameters used.** First, the simplifications in the descriptions of the hydrolysis of hydroxopolymers imply that all concentrations M_n are equal when $KW = C$, which corresponds to the region of $[H_2O] \approx 35$ mol L^{-1}. Second, the accepted law of the change in the reactivity $n(n-1)(n-2)$ of hydroxopolymers containing n water molecules in the coordination sphere also has an approximate character, and its error increases for high n values. That is why we restricted our consideration to $m = 5$, since when $m > 5$ the theoretical dependences are qualitatively different and have two pronounced maxima. The next conclusion from theoretical considerations is that the formation of hydrazine involves short hydroxide chains. This is confirmed by the fact that in the initial period of the reaction (10—30 s) the yield of N_2H_4 with account for stoichiometry of the reaction approaches a quantitative yield.[11] This is in accordance with concepts on the regularities of the formation of hydroxides,[1] according to which at first low-nuclear hydroxopolymers with not more than ten units forming the primary globule grow rapidly; processes of structural formation usually resulting in fast loss of nitrogen-fixation activity occur in these globules.

As a whole, this study confirms the hypothesis that a hydride mechanism is responsible for hydrazine formation. According to this mechanism, the concentration of the anionic charge at a small fragment of the $[Nb(OH)_3]_m$ hydroxo polymer results in the dissociation of coordinationally bound water with elimination of OH^- (Scheme 2).

Scheme 2



In the coordination sphere of Nb^{III}, a proton accepts an electron pair and gains hydride properties. This is accompanied by an increase by unity in the formal degree of oxidation of two metal atoms, while the reductive properties of the whole hydroxo cluster are retained.

At the rate-determining stage of the reaction, in the polynuclear hydride-nitrogen niobium complex, a H atom is transferred to the coordinated N_2 molecule to form a N—H bond, and the complex undergoes additional reduction due to the oxidation of two Nb^{III} ions to Nb^{IV}. Since one metal atom possessed a coordination vacancy before it is occupied by a solvent molecule, a leaving H atom remains partially bound to the metal atom (Nb···H—N) similarly to the agostic interaction of C—H bonds.

Thus, the four-electron reduction of the N_2 molecule occurs in the elementary stage (Scheme 3). This removes known difficulties that occur in multielectron processes and supports a high rate of the reaction.*

The hydrolysis of Nb—N bonds results subsequently in the formation of hydrazine (Scheme 4).

The mechanism presented (see Schemes 2—4) is confirmed not only by the kinetic scheme, which describes rather completely all of the reactions that occur,

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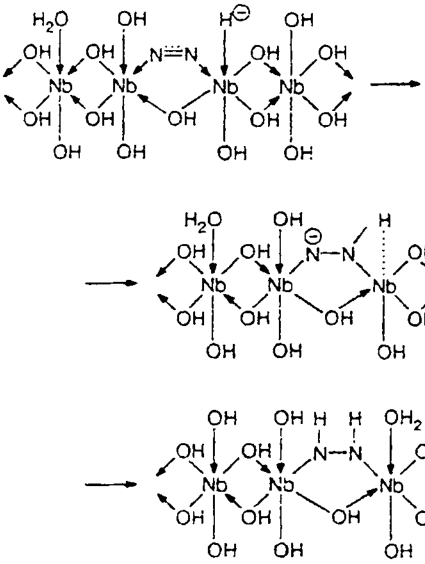
* The determined values of K_s are higher than those used previously,[8] which is caused by taking into account (see Ref. 2) only those hydrolytic equilibria in which the content of water molecules in the coordination sphere of ions changes only by unity. However, the K_s ratio obtained for the deuterated and protic solvents (1.27) is fairly close to the value of 1.33 calculated in terms of the previous model.

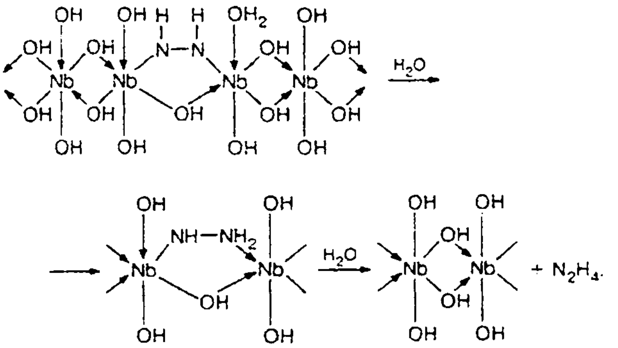
** The experimental data can be entirely described in terms of the accepted kinetic scheme when the number of parameters is slightly increased.

* The charges at the H and N atoms are indicated in Scheme 2 in order to emphasize a nonradical character of the formation of the corresponding intermediates.

Scheme 3



Scheme 4



but also by the fact that it explains other transformations observed in the system, *i.e.*, evolution of H_2

$$[L_xNb{-}H]^{(n-1)-} \xrightarrow{H_2O} [L_xNb{-}OH]^{n-} + H_2$$

and isotopic exchange of D_2 with the $H_2O{-}MeOH$ solvent, because according to modern concepts.[13,14] the reaction of D_2 with hydride metal complexes is one of the mechanisms of the formation of HD.

Thus, we developed a theoretical description of the effect of water on the nitrogen-fixation ability of hydroxide systems over Nb^{III}-containing systems. Unlike previous works, taking into account equilibria involving the solvent made it possible to describe the change in kinetic parameters in a wide range of water concentrations. The approach developed, which takes into account the particular composition of strongly solvated particles, seems to be sufficiently universal for studying the effect of the ratio of the components of the solvent on the rates of the chemical transformations in which they directly participate.

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