Two-path reduction of molecular nitrogen by transition metal hydroxides

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The kinetics of the reduction of N_2 to N_2H_4 and NH_3 by Ti^{III}—Mo^{III} hydroxide was studied at pH 11 and 303—333 K, and the activation energies for these reactions and also for the reaction $N_2H_4 \rightarrow 2\ NH_3$ were determined (29, 70, and 25 kJ mol^{-1}, respectively). It was concluded that ~90 % of ammonia was formed by the direct reduction of N_2 without intermediate formation of hydrazine. A mechanism of this reaction is suggested, which includes the proton insertion into the N—N bond favored by an enhanced electron density at the nitrogen atoms, according to the data of the quantum-mechanical calculation.

Key words: molecular nitrogen, ammonia; hydroxide; mechanism, reduction.

One of the interesting properties of the reduction of molecular nitrogen by transition metal hydroxides is a strong effect of pH of the medium on the reaction rate and the composition of the products.[1—3] Ammonia is the predominant or sole reaction product in weakly alkaline media (pH ~12), while hydrazine dominates in strongly alkaline media (pH ~14). This regularity, which was observed in all cases, made it possible to assume that nitrogen directly reduces to ammonia in weakly alkaline media, and in strongly alkaline media it reduces *via* the intermediate formation of hydrazine. To confirm this assumption, the kinetics of the reduction of hydrazine is usually studied additionally at various pH values, and the rate constant of this reaction is determined and compared to the rate of the ammonia formation observed experimentally (v_{NH_3}). As a rule, the experimental values of v_{NH_3} are several times greater than the calculated rate[3] determined by the reaction rate constant

$$N_2H_4 \rightarrow 2\ NH_3 \qquad (1)$$

and observed concentrations of hydrazine. This is evidence in favor of the fact that the majority of ammonia is not formed due to the reduction of hydrazine. However, despite the validity of this approach, the data obtained have only an estimate, because they do not take into account the effect of hydrazine, which is present in the reaction medium at the moment of the formation of hydroxide, on the reactivity of the latter. At the same time, the existence of different paths of nitrogen reduction can be obtained from the comparison of the values of activation energies of the formation of hydrazine ($E_{N_2H_4}$) and ammonia (E_{NH_3}) in the same series of experiments. This comparison was not performed previously. In this work, the values of the activation energies of both reactions were determined for the reduction of molecular nitrogen by the $Ti(OH)_3$—$Mo(OH)_3$ system. These values were compared, which allowed one to draw the correct conclusion about the existence of the two-path reduction of an N_2 molecule.

Experimental

Nitrogen was reduced in a three-chamber glass vessel[4] placed in an autoclave by the previously described procedure[5] at $[TiCl_3] = 5 \cdot 10^{-2}$ mol L^{-1}, $[MoOCl_3] = 5 \cdot 10^{-3}$ mol L^{-1}, $[KOH] = 10^{-3}$ mol L^{-1}, $p_{N_2} = 8$ MPa, H_2O — 5 vol. %. Hydrazine was reduced in an argon atmosphere, when the desired amount of a solution of hydrazine hydrate in methanol was added to the reaction mixture. Hydrazine was determined photocolorimetrically by its color reaction with *p*-dimethylaminobenzaldehyde,[6] and ammonia was determined by the indophenol method.[7]

Results and Discussion

The kinetic curves of the formation of hydrazine and ammonia, the products of the nitrogen reduction by Ti^{III} — Mo^{III} hydroxide at 303—333 K, are presented in Figs. 1 and 2. The values of the initial rates of formation of these products were used to determine the activation energies (Fig. 3, lines *1* and *2*). According to these data, $E_{N_2H_4} = 29(\pm 4)$ kJ mol^{-1} and $E_{NH_3} = 63(\pm 6)$ kJ mol^{-1}. It is noteworthy that at a low concentration of alkali, the value of the activation energy of the formation of hydrazine (29 kJ mol^{-1}) coincides with $E_{N_2H_4}$ determined at pH ~14, which points to the same mechanism of the formation of hydrazine. According to the data of Fig. 4, which presents the kinetic curves of the consumption of hydrazine at different temperatures, the activation energy of the reduction of hydrazine to ammonia is equal to 25 kJ mol^{-1}.

It was established from the kinetic curves (see Figs. 1, 2, and 4) that only 9—10 % of the amount of hydrazine

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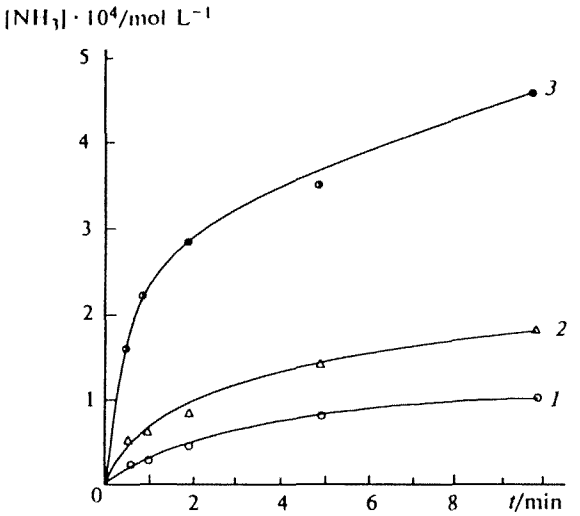


Fig. 1. Kinetic curves of the formation of ammonia at 303 K (*1*), 313 K (*2*), and 333 K (*3*).

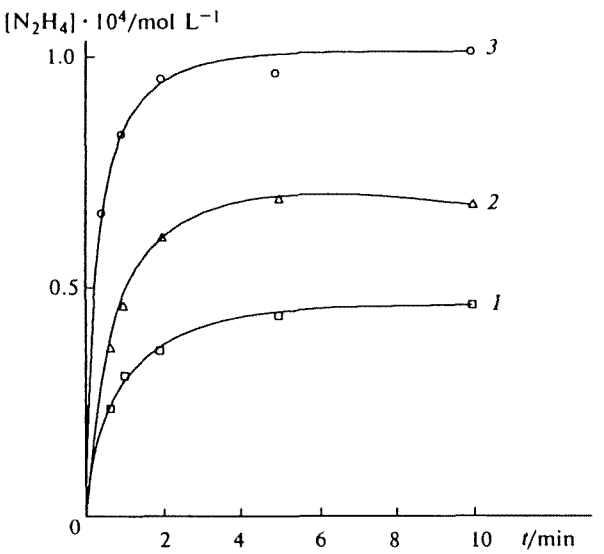


Fig. 2. Kinetic curves of the formation of hydrazine at 303 K (*1*), 313 K (*2*), and 333 K (*3*).

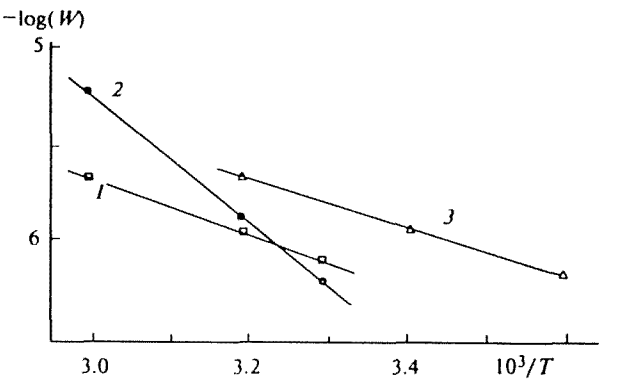


Fig. 3. Dependences of $\log(W)$ on T^{-1} for the reduction of nitrogen to hydrazine (*1*) and ammonia (*2*) and reduction of hydrazine to ammonia (*3*) according to the data of Figs. 1, 2, 4.

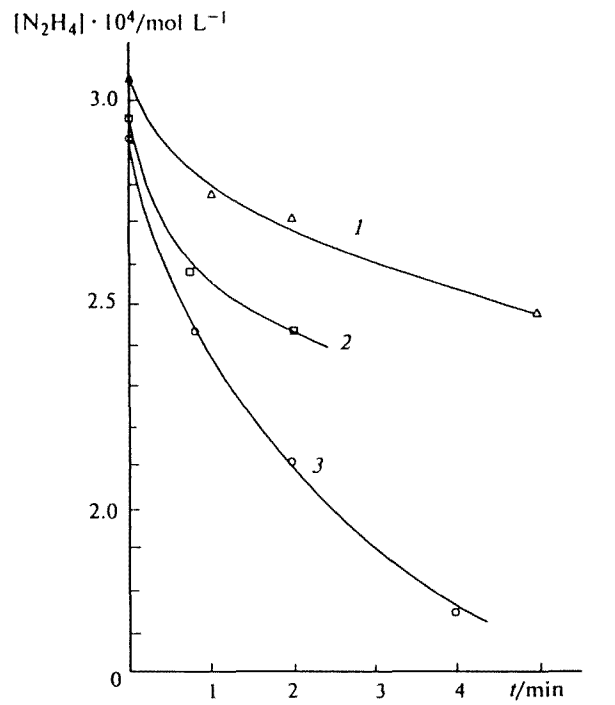


Fig. 4. Kinetic curves of the consumption of hydrazine at 277 K (*1*), 293 K (*2*), and 313 K (*3*).

formed corresponds to k_{eff} in reaction (1). It can be assumed that the real value of E_{NH_3} is ~70 kJ mol^{-1}.

The previously mentioned[8] peculiarity of the structure of a nitrogen molecule should be taken into account for further discussion: the high strength of the N≡N bond (946 kJ mol^{-1}), along with the abnormal high value of the first of the cleaved bonds (527 kJ mol^{-1}), is favorable only for multielectronic reactions accompanied by the cleavage of two or all three bonds of the N_2 molecule under mild conditions.

The value of the activation energy of the reaction is related in the first approximation to the extent of compensation of new bonds formed instead of the cleaved bonds. Therefore, in considering the subsequent process of the nitrogen reduction

$$N_2 \rightarrow N_2H_4 \rightarrow 2\ NH_3,$$

it can be expected that the activation energy of the hydrazine formation should be higher than that of the formation of ammonia from hydrazine, because the weakest bond is cleaved at the last stage, and the strongest bond is cleaved at the first stage.

It follows from these data that this dependence is not fulfilled: by the contrary, $E_{NH_3} > E_{N_2H_4}$. This indicates

that at a low concentration of alkali the formation of the majority of ammonia is not associated with the reaction of successive reduction of nitrogen, but it is caused by the individual independent pathway

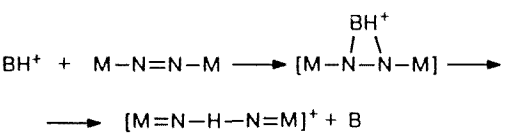
$$N_2 \rightarrow 2\ NH_3.$$

It can be mentioned that the direct reduction of nitrogen to ammonia was found in 1980,[1] but possible mechanisms of this reaction were never discussed.

The direct reduction of nitrogen to nitride in the binuclear Mo^{III} complexes in aprotic media has been described in the previous work.[9] However, a protic medium always introduces basic differences in the mechanism of the reduction of the nitrogen molecule, because the molecules of a solvent and base OR^- (R = H, Me) are the direct participants of this process. Therefore, the formation of readily hydrolyzed nitrides contradicts the high sensitivity of the reaction rate toward pH and slight changes in the composition of the solvent. In addition, in the Ti^{III}—Mo^{III} system, the degree of oxidation of molybdenum changes only by two units, and the formation of nitride $\geqslant Mo^{VI}$—N becomes impossible.

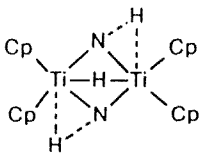
The simplest possibility of the multielectronic reduction of the nitrogen molecule without the intermediate formation of the hydrazine derivative is realized upon the direct insertion of a proton into the N—N bond of the coordinated N_2 molecule (Scheme 1).

Scheme 1



B is base.

Since the formation of ammonia is observed in weakly alkaline solutions, a molecule of a solvent can act as BH^+. The reduction and hydrolysis of the complex with the bridged proton in subsequent reactions can result only in the formation of ammonia. No direct analogs of this complex are known, but the existence of the stable complex with the internal hydrogen atom obtained directly from ammonia should be mentioned.[10]



To elucidate the possibility of the direct protonation of the N_2 molecule, we performed *ab initio* quantum-chemical calculations* of the insertion of H^+ into the N—N bond for systems $H^+ + N_2$ and $H^+ + N_2^{2-}$ (or $H^- + N_2$) using the HF/3-21G* and MP3/6-311G** methods for the geometry optimization.

The results presented in Table 1 show (*cf.* the ΔE values for two types of the NHN^+ structure) that the insertion of a proton into the nitrogen—nitrogen bond is strongly facilitated as the electron density on the nitrogen molecule increases. This corresponds to the thermodynamic factor: the loss in energy upon the proton insertion into the nitrogen molecule caused by the higher strength of the N—N bond (9.76 eV compared to the N—H^+ bond, 3.39 eV) decreases as the

* All calculations were performed by the GAUSSIAN-80 program adopted for EC-1045, version 4.2 (A. A. Gorbik and A. S. Zyubin, Institute of New Chemical Problems of the RAS, Chernogolovka).

Table 1. Results of optimization of selected states for N_2H^+ and N_2H^-

Method	*E* (au)	*r*(N—N)/Å	*r*(N—H)/Å	Δ*E*/eV	*E* (au)	*r*(N—N)/Å	*r*(N—H)/Å	Δ*E*/eV
		N_2+H^+				N_2+H^-		
HF/3-21G*	−108.39257	1.0750	∞	0.0	−108.79299	1.0950	∞	0.0
MP3/6-311G**[a]	−109.28601	1.0750	∞	0.0	−109.77262	1.0950	∞	0.0
MP3/6-311G**	−109.28726	1.0947	∞	0.0	−109.77387	1.0947	∞	0.0
		$NHN^+(D_{\infty h})$				$NHN^-(D_{\infty h})$		
HF/3-21G*	−107.89092	1.8540	0.9270	13.650	−108.39619	2.0562	1.0281	10.797
MP3/6-311G**[a]	−109.74975	1.8540	0.9270	12.619	−109.43831	2.0562	1.0281	9.097
MP3/6-311G**	−108.80492	1.5666	0.7833	13.125	−109.43988	2.1266	1.0633	9.088
		$NHN^+(C_{2v})$				$NHN^-(C_{2v})$		
HF/3-21G*	−108.50978[b]	1.0984	1.2896	−3.189	−108.60760	1.3776	1.1876	5.045
MP3/6-311G**[a]	−109.40858	1.0940	1.2692	−3.335	−109.62980	1.3776	1.1876	4.072
MP3/6-311G**					−109.62388	1.3475	1.1660	4.081

Note. *E* is the total energy of the system; Δ*E* is the difference in energies.
[a] For the geometry at the HF/3-21G* level. [b] Optimization in the 6-311G** basis.

electron density on the nitrogen molecule increases due to the following reasons: weakening of the $N^{\delta-}—N^{\delta-}$ bond and an increase in the strength of the $H^{+}—N^{\delta-}$ bond, which reaches 18.5 eV in the limiting case ($\delta = 1$). The appearance of two electrons in the nitrogen molecule results in a decrease in the absolute value of the barrier for the proton insertion into the N—N bond and decreases by more than three times the relative value of the barrier: the difference in energies of two structures, the preliminary $\overset{N}{\underset{N}{\parallel}}\!>\!H(C_{2v})$ and linear complexes [N—H—N]($D_{\infty h}$). It can be assumed that on going to the binuclear complexes in Scheme 1, the N—M interaction will result in a considerably higher stabilization of the structure $D_{\infty h}$ compared to the C_{2v} structure due to an increase in the unsaturated valency of its nitrogen atom. This provides qualitatively a decrease in the activation barrier for the proton insertion to appropriate values.

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