CHEMICAL FIXATION OF MOLECULAR NITROGEN BY AQUEOUS SOLUTIONS OF TRANSITION-METAL COMPOUNDS

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Abstract

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CHEMICAL FIXATION OF MOLECULAR NITROGEN BY AQUEOUS SOLUTIONS OF TRANSITION-METAL COMPOUNDS

Recently several works have been published devoted to the fixation of molecular nitrogen by comparatively simple chemical systems under mild conditions ([1–5]). Chatt and Scott ([1]) showed that small amounts of molecular nitrogen are fixed by hydrochloric-acid solutions of molybdate and tungstate in the presence of activated hydrogen and strong reducing agents.

Vol' pin and Shur ([2–4]) succeeded in fixing considerable amounts of molecular nitrogen with compounds of transition metals (titanium, molybdenum, tungsten, iron, and chromium) in nonaqueous solutions in the presence of such reducing agents as RMgBr (where $R{-}CH_3$, C_2H_5, $C_6H_5CH_2$, etc.) and $LiAlH_4$.

It was of interest to determine the possibility of fixing molecular nitrogen in simple systems (acidic aqueous solutions) by compounds of transition metals of the fourth, fifth, sixth, and seventh groups of the periodic system of D. I. Mendeleev.

In all experiments acidic solutions, 3 N in HCl or 4 N in H_2SO_4, containing $1{\cdot}10^{-3}$ mole/liter of transition-metal compounds were used. Metallic zinc (chemically pure grade) or zinc amalgam (zinc content in the amalgam 2.5%) was used as reducing agents. All reagents were first checked for the content of nitrogen compounds in them. In the reaction vessel circulation of nitrogen was ensured through a sealed-in porcelain porous filter. Nitrogen was passed for 6 hr, being purified from oxygen by means of copper turnings at 600–700°. It had previously been established that the maximum amount of fixed nitrogen was obtained after 6 hr. Into the reaction vessel 50 ml of the above solutions were first introduced and, after a 10-minute passage of nitrogen, two portions of metallic zinc were added (2 g each after 3 hr). At the end of the experiments, samples (20 ml each) were taken to determine bound nitrogen. The sample was alkalized with 20 ml of 50% KOH, and ammonia was distilled with steam into a receiver containing 10 ml of 0.01 N HCl. The distilled samples were neutralized with 1 ml of 0.1 N KOH, and the content of NH_4^+ ion was determined colorimetrically with Nessler' s reagent. In all cases parallel experiments were carried out with

Figure 1

Figure 1: Figure 1

solutions containing all components except transition-metal compounds.

Experiments with zinc amalgam were carried out in ordinary bubblers; the volume of the solutions under study was likewise 50 ml, and the volume of zinc amalgam 10 ml. All other conditions for carrying out the experiments, sampling, and sample analysis were analogous. The experiments were conducted at room temperature and atmospheric pressure. The experimental results obtained are given in Table 1.

Consideration of the data given in Table 1 shows that nitrogen fixation occurred in solutions containing reducible compounds of titanium, vanadium, niobium, molybdenum, tungsten, and rhenium. In solutions of zirconium, hafnium, and tantalum, which are not reduced under the conditions of our experiment, chemical fixation of nitrogen was not observed. The results in the case of applying compounds of Cr III and Cr VI proved—

turned out to be different. Namely, in the presence of Cr(III) compounds there is no nitrogen fixation, whereas in the case of Cr(VI) compounds a noticeable amount of fixed nitrogen was observed. Nitrogen fixation was also absent in hydrochloric-acid solutions of Mn(II).

The data presented show that chemical fixation of nitrogen takes place in solutions containing compounds of transition elements with a small number of *d*-electrons. Syrkin expressed the view (^{6}) that chemisorption of molecular nitrogen on transition metals may be explained by the formation of three-center bonds: donor–acceptor bonds involving the pair of electrons of the nitrogen π-bond and vacant *d*-orbitals of the metal, and dative bonds involving the metal *d*-electrons and the antibonding orbitals of the nitrogen molecule. For formation of a π-complex with nitrogen, as is known, it is also necessary that the transition-metal atom possess free antibonding *d*-orbitals interacting with the filled π-bonding orbitals of nitrogen, and filled nonbonding *d*-orbitals of the metal overlapping with the vacant antibonding π-orbitals of the nitrogen molecule. Consequently, it is necessary that the metal atom entering the compound have a certain number of *d*-electrons, but that vacant *d*-orbitals remain. From this point of view the "best" electronic configurations of transition metals could include the configurations d^1, d^2, d^3.

Fig. 1. Dependence of the amount of fixed nitrogen on the concentration of $KReO_4$ (1) and Na_2MoO_4 (2) in 3 N HCl medium. Reducing agent—zinc amalgam

Table 1

Fixation of molecular nitrogen in hydrochloric-acid and sulfuric-acid solutions in the presence of transition-metal compounds ($1 \cdot 10^{-3}$ mol/l)

(amount of NH_4^+ ion in mol. % based on the initial salt of the transition metal)

In hydrochloric-acid solutions (3 N HCl), reducing agent—zinc amalgam		In hydrochloric-acid solutions (3 N HCl), reducing agent—metallic zinc		In sulfuric-acid solutions (4 N H_2SO_4), reducing agent—zinc amalgam	
compounds	NH_4^+-ion	compounds	NH_4^+-ion	compounds	NH_4^+-ion
$TiCl_4$	3.4	$K_2Cr_2O_7$	2.1	Na_2MoO_4	2.3
$ZrOCl_2$	0.0	Na_2MoO_4	2.7	Na_2WO_4	2.4
$HfOCl_2$	0.0	Na_2WO_4	2.6	$KReO_4$	0.0
$VOSO_4$	3.1	$KReO_4$	4.1		
$NbCl_5$	2.5	$KMnO_4$	0.0		
$TaCl_5$	0.2				
$K_2Cr_2O_7$	2.0				
$CrCl_3$	0.0				
Na_2MoO_4	2.2				
$NaWO_4$	3.4				
$KReO_4$	1.3				

As can be seen from the data in Table 1, the nature of the acid (HCl and H_2SO_4) has no substantial effect on the fixation of molecular nitrogen, nor does the nature of the reducing agent (zinc or zinc amalgam). Only in the case of rhenium compounds, which are reduced in sulfuric-acid medium to lower oxidation states (below two) (^{7}), was no nitrogen fixation observed.

It is also important to note that the amount of fixed molecular nitrogen depends on the concentration of transition-metal compounds in the solutions studied. The corresponding experiments were carried out with rhenium and molybdenum compounds. The concentration of the latter was varied within the range-

···in the range from 10^{-6} to 10^{-2} mol/l. The specified experimental conditions, such as acidity (3 N HCl), reducing agent (10 ml of 2.5% zinc amalgam), and duration of the experiments (6 h), were kept constant.

It follows from Fig. 1 that the maximum amount of molecular nitrogen is fixed at a perrhenate and molybdate concentration equal to $1 \cdot 10^{-4}$ mol/l. With a further increase, as well as with a decrease, in the concentration of the transition elements, a sharp decrease is observed in the amount of fixed molecular nitrogen. The causes of these phenomena are at present difficult to explain completely; however, they are probably connected not only with the solubility of nitrogen in the systems studied ($5 \cdot 10^{-4}$ mol/l), but also with the state of the transition-metal compounds in these solutions (with the possible formation of polynuclear complexes, hydrolysis, etc.).

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