# THE REDUCTION OF ACETYLENE BY COMPLEXES

A. G. Ovcharenko, A. E. Shilov, and L. A. Nikonova UDC 542.941.7:547.314.2

As is well known, one of the peculiarities of nitrogenase is its ability to reduce unsaturated compounds with a triple bond: acetylene, azides, nitriles, nitrous oxide. The reaction with  $C_2H_2$  leads to the formation of ethylene; no further reduction to ethane occurs. In the presence of  $D_2O$ , cis-dideuteroethylene is formed [1].

In [2] a homogeneous system [aqueous alkaline solutions of V(II) with pyrocatechol (PC)], which reduces  $C_2H_2$  to ethylene at ~20° and atmospheric pressure, was described. In the reactions of this system, certain features of similarity to nitrogenase can be noted. Actually,  $C_2D_2$  is reduced to cis-dideuteroethylene in  $H_2O$ . Moreover, under certain conditions nitrogen is reduced to NH<sub>3</sub> under mild conditions in the presence of a complex of V(II) with PC [3, 4].

In order to determine the role of V(II) in these complexes and to study other such systems, we investigated complexes of PC with other transition metals in a low valence state. This article presents the results of a study of the reduction of  $C_2H_2$  by pyrocatechol complexes of Ti(III), Cr(II), and Mo(III).

### EXPERIMENTAL METHOD

 $VSO_4 \cdot 7H_2O$  and  $K_3MoCl_6$  were produced by electrochemical reduction of  $VOSO_4$  and  $MoO_3 \cdot CrCl_2$  was synthesized according to the method of [5]. Acetylene was purified by refreezing under vacuum; the purity was monitored by the method of gas -liquid chromatography (Tsvet-1000 chromatograph, model 104). PC was purified by sublimation under vacuum. Acetylene was reduced in Rittenberg vessels, in which solutions of metal salts with PC (volume of the liquid phase 20 ml) were mixed with buffer solutions in a stream of  $C_2H_2$ ; the yield of ethylene and ethane was measured chromatographically after 24 h in all cases.

The concentrations of V and Ti were determined on an FÉK-56 colorimeter with No. 4 ( $\lambda_{max}$ 434 nm) and No. 3 ( $\lambda_{max}$ 400 nm) light filters. The CrCl<sub>2</sub> concentration was determined iodometrically, while the Mo(III) concentration was determined by back titration of the excess K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> with Mohr's salt. In the experiments with <sup>15</sup>N<sub>2</sub>, the analysis was conducted mass spectrometrically by the method of isotopic dilution. The isotopic composition of ethane in the experiments with C<sub>2</sub>D<sub>4</sub> + C<sub>2</sub>H<sub>2</sub> was determined on an MKh-1302 mass spectrometer. The mass spectra were calculated according to the data of [6].

## DISCUSSION OF RESULTS

Like V(II), the compounds of Ti(III), Cr(II), and Mo(III) form soluble complexes with PC, which do not decompose liberating hydroxides even in concentrated alkaline solutions. The complexes of V(II), Ti(III), and Mo(III) gradually decompose water, liberating  $H_2$ . Acetylene is reduced in solutions of these complexes, and the reaction begins at pH > 5 (Fig. 1). The basic product in all cases is ethylene; the reaction proceeds according to the stoichiometric equation

$$2M^{n+} + C_{2}H_{2} + 2H_{2}O \rightarrow 2M^{(n+1)+} + C_{2}H_{4} + 2OH^{-}$$
<sup>(1)</sup>

In the reduction of  $C_2H_2$  by complexes of V(II) and Mo(III), together with ethylene, a certain amount of ethane is obtained. With complexes of V(II) ethane is formed only in strongly alkaline solutions ([KOH] ~ 2 M) (Fig. 2); with complexes of Mo(III) it is already formed at pH  $\approx 5$  (see Fig. 1). It can be noted

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Fig. 1. Dependence of the yield of ethylene on the pH of the solutions in the reduction of acetylene by metal complexes with pyrocatechol: 1) V:PC = 1:71; 2) 1:50; 3) 1:10; 4) [Mo(III)] 0.004 M, [PC]<sub>0</sub> 0.090 M; 5) yield of ethane.

Fig. 2. Dependence of the yield of ethylene (1) and ethane (2) on the pyrocatechol concentration in the reduction with complexes of V(II) with pyrocatechol,  $[VSO_4]_0 = 0.048 \text{ M}$ ,  $[KOH]_0 = 2 \text{ M}$ .

that the yield of ethylene in the reduction of  $C_2H_2$  with complexes of Cr(II) is quantitative [calculated on the basis of the consumption of Cr(II) according to Eq. (1)], while in the case of reduction by Mo(III) complexes it is smaller.

The reactions studied proceed very rapidly with complexes of V(II), and substantially more slowly in the reactions of the remaining reducing agents. Experiments on the reduction of ethylene in aqueous and methanol solutions were conducted under conditions analogous to the reduction of  $C_2H_2$ . In all cases the formation of ethane was observed (Table 1). As can be seen from Table 1, in methanol solutions, in comparison with aqueous solutions, somewhat more ethane is formed, which can be explained by the better solubility of ethylene in methanol.

In order to determine the stereospecificity of the reduction of  $C_2H_2$  we conducted experiments with  $C_2D_2$  at pH 10 in strongly alkaline solutions ([KOH] ~ 2 M) at a ratio M : PC = 1:10. In the reaction with V(II), cis-dideuteroethylene is formed, and with Ti(III) a mixture of cis- and trans-isomers; with Cr(II) and Mo(III) only the trans-isomer is formed. The results at the two pH values studied are qualitatively analogous.

Several experiments were conducted in order to determine the possibility of reduction of molecular nitrogen. To avoid errors on account of ammonia impurities, the experiments were conducted in  ${}^{15}N_2$ . It was found that in all cases except for V(II), the isolated NH<sub>3</sub> does not contain  ${}^{15}N$ , i.e., no fixation of nitrogen occurs. The reduction of nitrogen in a solution of the complex of V(II) with PC was studied in [4].

To determine the pathway of formation of ethane in the system V(II)-PC, experiments were conducted in the joint presence of  $C_2H_2$  and  $C_2D_4$  (in a 1:8 ratio), in which the concentrations of both gases in solution were approximately the same. Chiefly  $C_2H_6$  is formed in the reaction products, which indicates a direct reduction of  $C_2H_2$  to ethane without leaving the coordination sphere of the complex.

It is difficult to draw more definite conclusions from the data obtained on the detailed mechanism of the reaction that we detected. It can be assumed that the reaction with  $C_2H_2$ , just as in an acid solution of Cr(II) salts [7], proceeds through the formation of an intermediate binuclear complex. However, in contrast to Cr(II), in this case the transition not only  $V(II) \rightarrow V(III)$ , but also  $V(II) \rightarrow V(IV)$  is possible; in a binuclear complex, the latter transition can lead to the reduction of  $C_2H_2$  to ethylene according to a cisscheme and to the reduction of  $C_2H_2$  to ethane:

$$2V^{2+}+4H_2O+C_2H_2 \rightarrow 2V^{4+}+C_2H_6 + 4OH^-$$

Possibly this reaction actually occurs in a series of steps, for example,

TABLE 1

м	Solvent	[M] *	[PC]	[кон]	[C2H8]	[C2H3]/[M], %
v	Water Methanol	0,049	0,485	0,504	1,3.10-4	35,5
Ti	Water Methanol	0,048 0,048	0,485 0,485	0,504 0,504	4,0.10-5	11,0 27,5
Cr	Water " Methanol	$0,047 \\ 0,045 \\ 0,045$	$0,470 \\ 0,450 \\ 0,470$	0,470 1,81 1,90	2,5·10-5 3,5·10-5 3,5·10-5	5,3 7,4 7,4
Мо	Water Methanol	0,004 0,004	0,100	2,18	2,4.10-5	12,2 24,4

\*[M] is the concentration of the metal complex. M.



### CONCLUSIONS

1. The reduction of acetylene by complexes of transition metals [V(II), Ti(III), Cr(II), Mo(III)] in the presence of pyrocatechol at various pH of the solutions was studied.

2. In the reaction of deuteroacetylene with V(II), cis-dideuteroethylene is formed, with Ti(III) a mixture of the cis- and trans-isomers, and with Cr(II) and Mo(III) only the trans-isomer.

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