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REDUCTION OF CYANIDE AND ACETONITRILE BY PROTON NIGROGEN-
FIXATION SYSTEMS

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The physiological function of the enzyme nitrogenase consists in the reduction of N_2 to NH_3 but, in the fermentation system, it is also possible to observe a number of other reduction reactions [1]. For instance, HCN or CN^- which is in equilibrium with it, gives mainly six-electron reduction products, although a little methylamine is formed simultaneously

$$CN^- + 6e + 7H^+ \rightarrow CH_4 + NH_3 \qquad (1)$$

$$CN^- + 4e + 5H^+ \rightarrow CH_3NH_2 \qquad (2)$$

Acetonitrile is also reduced with the participation of six electrons to C_2H_6 and NH_3.

When the reactions of the enzyme nitrogenase and model proton nitrogen-fixation systems [2] were compared we studied the reaction of CN^- and CH_3CN in model systems based on V(II), Cr(II), and Ti(III).

EXPERIMENTAL

$VSO_4 \cdot 7H_2O$ was synthesized by electric reduction of vanadium sulfate. Hydrochloric acid solutions of $TiCl_3$ and $CrCl_2 \cdot 4H_2O$ were prepared by dissolving metallic Ti and Cr in aqueous HCl. The starting solutions were prepared and stored in a box with Ar and two- or three-component Rittenberg vessels in which the experiments were carried out were filled with them. The total volume of the aqueous reaction solutions or mixtures was usually 10 ml and their content of V(II), Ti(III), or Cr(II) was 0.5 mmole. The gaseous reaction products were separated by a Tepler pump and analyzed by GC or mass spectrometrically. To record the PMR spectra, using a Bruker SXP-4-100 spectrometer, the volatile reaction products were frozen in a well-pumped system in the receiver containing 1.5 ml of 0.1 N HCl and immersed in liquid nitrogen; the resulting solution was evaporated to dryness and the dry residue was dissolved in 0.6 ml of an 0.05 M solution of acetone in D_2O.

DISCUSSION

Catechol complexes with V(II) formed by mixing solutions of V(II) salts with alkaline solutions of catechol in water or methanol effeciently reduce N_2 and, in the absence of substrates, they react with the protons in the medium [2]

$$2V(II) + 2H^+ \rightarrow 2V(III) + H_2 \qquad (3)$$

KCN and acetonitrile, even with V(II)/substrate proportions of $\approx 2-3.5$, almost completely suppress reaction (3), which is comparatively slow at pH $\leqslant 13$. The yellow or red coloration of the complexes, generated by mixing aqueous solution of 0.5 mmole V(II), 5 mmole of pyrocatechol, and 5-8 mmole of NaOH (pH $\sim 10-13$), changes rapidly to green V(III) complexes when an 0.15 mmole solution of KCN or CH_3CN is added. The following results confirm the formation of methylamine from cyanide and ethylamine from acetonitrile. Both products diffuse readily from the reaction solutions and are absorbed by dilute solutions of acid at about 20°C; they are also frozen out together with the water. During chromatography on paper they have the same

R_f values as the corresponding amines taken as reference spots. The PMR spectra of the products are the same as those of $CH_3 \cdot NH_2 \cdot HCl$ (a singlet with δ 2.44 ppm) and $C_2H_5NH_2 \cdot HCl$ (a triplet with δ 1.11 ppm and a quadruplet with δ 2.89 ppm, with J = 7.6 Hz). The amine yields, determined by titration and calculated from the integral strengths of their PMR signals, agree satisfactorily; in all the experiments the yields are >85% calculated on V(II) for a type (2) reaction. There are no hydrocarbons in the reduction products of both substrates.

These substrates also behave similarly in aqueous heterogeneous systems based on $V(OH)_2$ and $V(OH)_2$—$Mg(OH)_2$ with pH $\leq$ 14. Thus, when the freshly prepared mixed hydroxide (from 0.5 mmole V(II), 2.5 mmole Mg (II), and 10 mmole NaOH) reacts with 0.15 mmole of CH_3CN about 85% is formed; when it reacts with 0.25 mmole of cyanide, 50% methylamine, 35% H_2, and 0.05% CH_4 are formed, no CH_2O being noticed.

The composition of the products in the system $V(OH)_2$—$Mg(OH)_2$—CN^- does not vary substantially also when changing to strongly alkaline aqueous—methanol media, although under these precise conditions in [3] a different trend of the reaction of cyanide was detected: total rupture of the C—N linkage with the formation of CH_2O and NH_3. According to the findings in [3], in the reaction solution, separated from the hydroxide precipitate by centrifuging, formaldehyde is determined qualitatively (analysis by chromotropic acid in H_2SO_4), while CH_2O is not detected in the control experiment (all components of the system except V(II)). By the same method of analysis CH_2O has been detected not only in the reaction with cyanide but also in experiments in which all the components of the system except cyanide were taken. Apparently, CH_2O is formed, not with the reduction of CN^-, but with the oxidation of CH_3OH by atmospheric oxygen (the solvent being 20% CH_3OH—H_2O) in a reaction coupled with oxidation of $V(OH)_3$ or during an analysis in the presence of traces of vanadium. In [3] no quantitative results are given on the colorimetric determination of NH_3 while the PMR method which we used clearly confirms the formation of methylamine as the principal product of the reduction of cyanide.

Unlike V(II), Cr(II) and Ti(III) do not react with N_2 in aqueous alkaline media; in aqueous methanol Cr(II) and Ti(III) show weak activity in this reaction (see [4], for example), but in the presence of molybdenum they efficiently reduce N_2 in both the solvents [2].

Cyanide gives about 30% methylamine, 5–15% CH_4, and a little H_2 in the presence of Cr(II) hydroxide in water at pH $\sim$ 10–13.5; methylamine is not an intermediate component in the formation of methane because, under these conditions, it is not reduced to CH_4. From acetonitrile on $Cr(OH)_2$ and in alkaline solutions of catechol complexes with Cr(II) ethylamine is formed in about 50% yield, the heterogeneous system containing in the products about 1% C_2H_6. The reaction of cyanide with $Ti(OH)_3$ and $Ti(OH)_3$—$Mo(OH)_3$ with pH $\sim$ 12.8 and a CN^-/Ti(III) ratio = 3 gives about 40% CH_3NH_2, $\sim$50% H_2, and 1–5% methane; acetonitrile under the same conditions forms 20–30% ethylamine, H_2, and traces of C_2H_6 and C_2H_4; in solutions of catechol complexes with Ti(III) at pH $\sim$ 12 and a CH_3CN/Ti(III) ratio = 1 about 40% ethylamine and 50% H_2 is formed. In weakly acid media neither HCN or CH_3CN oxidizes V(II), Ti(III), and Cr(II) over a prolonged period and they react only when the solutions are made alkaline.

Thus, in all the systems studied, unlike the enzymatic systems, the main reduction products of both the substrates are amines; noticeable quantities of hydrocarbons are only formed on Ti and Cr hydroxides. There is no correlation between the efficiency of the simulated system in fixing N_2 and the proportion of the products of four- and six- electron reduction of both the substrates investigated. As is evident from the results, the activity of the systems in the reduction of nitrogen does not mean that they will be obliged to simulate all the reactions of the enzyme. At the same time certain systems, for instance the molybdenum thiol system in [5], which exhibits slight activity in nitrogen fixation, reduce cyanide and acetonitrile catalytically to hydrocarbons and ammonia and in these reactions they simulate the action of the enzyme.

CONCLUSION

In proton nitrogen—fixation systems based on vanadium(II), chromium(II), and titanium(III) the principal reaction of cyanide and acetonitrile is four—electron reduction to methylamine and ethylamine.

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RELATIVE KINETICS OF $Mn_2(CO)_{10}$-INITIATED TELOMERIZATION

OF ETHYLENE BY METHYL TRI- AND MONOCHLOROACETATES

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UDC 541.127:66.095.2:547.313.2

An investigation of telomerization and addition initiated by dimanganese decacarbonyl and complex systems based on it makes it possible to note two peculiarities of $Mn_2(CO)_{10}$ as an initiator of reactions that proceed through cleavage of the C–Cl bond. The first peculiarity is the high effectiveness of $Mn_2(CO)_{10}$ in the step involving initiation of reactions with halogen-containing telogens. On the other hand, dimanganese decacarbonyl and systems based on it are active to a considerably lesser extent in the step involving chain propagation through the telogen at the C–Cl bond than complex initiating systems based on iron penta-carbonyl. This is seen most graphically in the case of the reaction of $CHCl_3$ with 1-hexene [1]. A rather high yield ($\sim50\%$) of adducts that contain a CCl_3 group is obtained in this reaction both in the presence of $Mn_2(CO)_{10}$ and in the case of initiation by the $Mn_2(CO)_{10}$ + dimethylformamide (DMF) system; at the same time, the fraction of compounds formed through chain propagation at the C–Cl bond of chloroform does not exceed 5%. The reaction proceeds basically in the same way as in the presence of peroxide initiators, i.e., through propagation at the C–H bond. The reaction of $CHCl_3$ with 1-heptene [2] initiated by $Fe(CO)_5$ + CH_3OH gives primarily an adduct with the $CHCl_2CH_2CHClC_5H_{11}$ structure, i.e., chain propagation takes place at the C–Cl bond.

The difference in the behavior of $Mn_2(CO)_{10}$ and the $Mn_2(CO)_{10}$ + DMF system was revealed during a study of the relative kinetics of telomerization of ethylene with CCl_4. A certain increase in all the C_n values (n = 1–3) was noted in the presence of $Mn_2(CO)_{10}$, while the $Mn_2(CO)_{10}$ + DMF system affects only the C_1 value, but to a considerably lesser extent than in the case of the $Fe(CO)_5$ + CH_3OH system [2].

In the present research we continued our study of the relative kinetics of reactions initiated by $Mn_2(CO)_{10}$ and $Mn_2(CO)_{10}$ + DMF. As the subjects of investigation for comparison of the peculiarities of the reaction at the C–Cl and C–H bonds we selected the telomerization of ethylene by methyl trichloroacetate and methyl chloroacetate. The telomerization of ethylene by methyl trichloroacetate initiated by $Mn_2(CO)_{10}$ proceeds via the usual scheme to give a number of $Cl(CH_2CH_2)_nCCl_2CO_2CH_3$ telomers (T_n^{Cl}). The partial constants for C_n chain propagation were determined in experiments carried out at 140°C in the interval M/S 0.3–3 (Table 1). The values obtained ($C_1 = 0.33$, $C_2 = 3.6$, and $C_3 = 5.5$) are higher by a factor of 1.5–2.5 than the analogous values determined in the presence of tert-butyl peroxide. At the same time, the ratio of the constants remained virtually unchanged, i.e., the use of $Mn_2(CO)_{10}$ for initiation did not have a substantial effect on the distribution of the telomer homologs. A different pattern was observed when the reaction was carried out in the presence of $Mn_2(CO)_{10}$ + DMF. This system is extremely effective as a chlorine-atom carrier in this reaction. The percentage of the first telomer reaches 70–90% (depending on the M/S ratio) of the sum of the telomers (Table 2). A comparison of the data in Tables 1 and 2 shows that the ratio of the yields of telomers is extremely sensitive to a change in the nature of the initiating system. An estimate of the C_1 value from the experiments in Table 2 gives a value of three to four, i.e., an order of magnitude higher than in the case of initiation with $Mn_2(CO)_{10}$ alone.