1,8-naphthoylene-1,2-benzimidazole (III), which can be regarded as the monocarbonyl analog of the model compound (I), does not give a green color when subjected to the action of $NaBH_4$, either with or without the presence of palladium, even though the transfer of electrons to (III) does take place [as a result of reaction of (III) with Na in THF]. This is indicated by the appearance of a signal in the EPR spectrum with hfs corresponding to the interaction of an unpaired electron with two nitrogen nuclei.

Thus, the changes in activity, selectivity, and phase composition of palladium catalysts for the hydrogenation of unsaturated compounds — changes that take place as a result of pretreatment with $NaBH_4$ — are related to processes of electron transfer to the support and, in particular, to reduction of the support to a leuco base. This base has a lower electron affinity than the original support, and this hinders transfer of electron density to the support from palladium atoms or clusters. A partial negative charge is probably created on the palladium under reducing conditions (as a result of treatment with $NaBH_4$). Such catalysts actually lose their ability to catalyze the hydrogenation of double bonds, thus manifesting high activity in the selective hydrogenation of alkynes to alkenes [10].

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CATALYTIC PROPERTIES OF POLYVANADOMOLYBDIC ACIDS IN OXIDATION OF 1,2,4-TRIMETHYLBENZENE BY PERACETIC ACID

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Polyvanadomolybdic acids catalyze the process of peracid oxidation of 1,2,4-trimethylbenzene. The selectivity with respect to 2,3,5-trimethyl-1,4-benzoquinone increases with increasing degree of replacement of vanadium atoms in the PVMA by molybdenum; this is related to increased stability of the intermediate peroxides of the heteropolyvanadates.

Investigation of the catalytic activity of mineral acids in the oxidation of 1,2,4-trimethylbenzene (TMB) by peracetic acid (PAA) has indicated low selectivity of these acids with respect to the desired product 2,3,5-trimethyl-1,4-benzoquinone (TMBQ), which is an intermediate in the synthesis of vitamin E [1, 2]. In the work reported here, we investigated the catalytic properties of polyvanadomolybdic acids (PVMAs) with the general formula $H_2V_{12-x}Mo_xO_{31\pm y}\cdot nH_2O$ in the process of TMB oxidation by peracetic acid.

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TABLE 1. Catalytic Activity of Polyvanadomolybdic Acids in Relation to Their Composition

Catalyst	$W_0 \cdot 10^4$, moles/(liter·sec)	TMB conversion, %	Selectivity for TMBQ, %
–	0,57	10,0	7,1
$H_2V_{12}O_{31}$	1,82	21,7	12,3
$H_2Mo_1V_{11}O_{31}$	1,14	16,7	24,0
$H_2Mo_2V_{10}O_{31}$	1,04	16,6	24,6
$H_2Mo_3V_9O_{31}$	0,98	16,0	28,8
$H_2Mo_4V_8O_{31}$	0,92	15,0	31,3

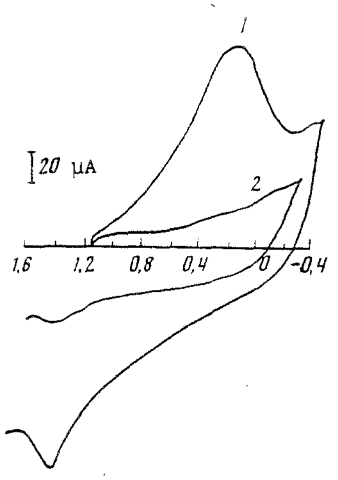


Fig. 1

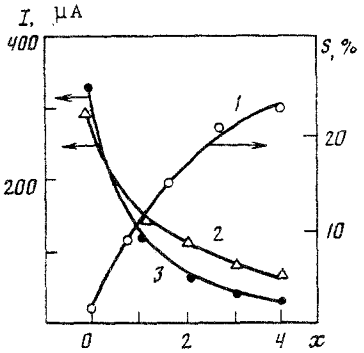


Fig. 2

Fig. 1. Cathodic–anodic polarization curves of compounds $H_2V_{12-x}Mo_xO_{31\pm y}\cdot nH_2O$ in 0.25 M H_2SO_4 with x = 0 (1) and 3 (2).

Fig. 2. Selectivity of TMB oxidation process (1), oxidation current with φ_a = 1.4-1.6 V (2), and reduction current with φ_k = 0.5-0.2 V (3) in 0.25 M H_2SO_4, as functions of molybdenum content in $H_2V_{12-x}Mo_xO_{31\pm y}\cdot nH_2O$ (x).

EXPERIMENTAL

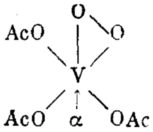
Samples of PVMA with the composition $H_2V_{12-x}Mo_xO_{31\pm y}\cdot nH_2O$, where $0 \le x \le 4.0$, $0.3 \le y \le 1.3$, and $8.0 \le n \le 10.0$, were obtained by a procedure given in [3], using starting materials that were of analytically pure grade. The compounds were checked by means of chemical analysis, thermal analysis, IR spectroscopy, and x-ray diffraction. The oxidation–reduction properties and chemisorption properties of the PVMAs in relation to oxygen were determined by an electrochemical method, using a carbon-paste electroactive electrode in a background of 0.25 M sulfuric acid [4].

The TMB used in this work was pure grade; the oxidizer was a 40% solution of PAA in acetic acid, obtained by a procedure given in [5]. The process was carried out in a glass reactor equipped with a stirrer and reflux condenser, at a temperature of 20°C with an oxidation period of 4 h. The reactor was charged with 0.6 g of the catalyst, 0.05 mole of TMB, and 40 ml of CH_3COOH; after thermostating, 0.1 mole of PAA was added. The reaction was terminated by adding 50-100 ml of distilled water to the reaction mass. The products of oxidation were extracted with chloroform and analyzed by GLC, using procedures described in [1].

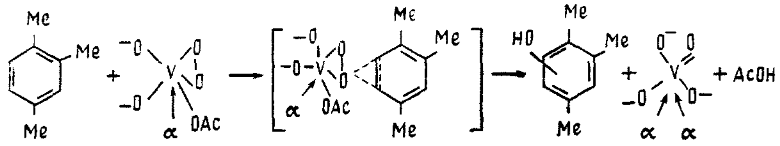
RESULTS AND DISCUSSION

The vanadium compounds have appreciable catalytic activities (Table 1). The shape of the kinetic curves for TMB consumption and TMBQ accumulation, as well as the variation of process selectivity for TMBQ as a function of the depth of substrate conversion, are similar to those observed in catalysis of the oxidation process by mineral acids or cation exchangers [1]. Replacement of these materials by PVMA did not bring about any changes in the composition of the oxidate. The acidic character of catalysis by PVMA is supported by PMR spectroscopic data in measuring the acid functions of the vanadium compounds under investigation. When vanadium atoms are replaced by molybdenum, the H_3O^+ number drops from 2 to 1.1, symbatic to the change in values of W_0 and substrate conversion; a considerable increase in the process selectivity for TMBQ is observed (Table 1).

As was shown in [1], the oxidation of TMB by peracetic acid is a complex process that includes a number of parallel and consecutive reactions. The TMBQ selectivity depends on the ratio of rates of the consecutive reactions of TMB hydroxylation and oxidative splitting of TMBQ. In studying the oxidation of TMBQ by peracetic acid in the presence of PMVA, it was found that the initial rate of the process was very similar for all of the samples, $W_0 \approx 1.8 \cdot 10^{-6}$ mole/(liter·sec). Thus, the change in process selectivity for TMBQ is a consequence of a difference in TMB hydroxylation rates. The catalytic effect of PVMA in the hydroxylation process is apparently related not only to the acidity (the acidity of PVMAs containing from 1 to 4 Mo atoms does not vary significantly), but also to their oxidizing and reducing properties. It is known that, in a peroxide medium, vanadium compounds form highly active peroxo compounds [7]. The formation of peroxo compounds of vanadium in the decomposition of PAA in acetic acid in the presence of oxide compounds of vanadium was established in [8]. Peracetic acid decomposes exclusively through the formation of an intermediate peroxo complex



The stability of such complexes of PVMAs is a function of their oxidizing and reducing properties, which can be evaluated by electrochemical techniques. According to the voltammetric polarization curves that were obtained (Fig. 1), PVMAs are readily oxidized and reduced; with increasing degree of replacement of V by Mo, the quantity of weakly bound oxygen decreases, with a corresponding increase in the quantity of chemically bound oxygen, as indicated by the magnitude of the current $\varphi_k = 0.5\text{-}0.2$ V and $\varphi_a = 1.4\text{-}1.2$ V [9]. The change in magnitudes of these currents correlates well with the increase in selectivity of TMB oxidation to TMBQ (Fig. 2). The role of molybdenum apparently consists of stabilization of the peroxo compounds of vanadium as a result of the higher energy of the oxygen bond in $H_2V_{12-x}Mo_xO_{31 \pm y} \cdot nH_2O$ as its quantity increases in the PVMA. With increasing stability of the intermediate peroxo compound of vanadium, its concentration in the reaction mass increases, accompanied by an increase in the rate of the catalytic pathway that limits this process of electrophilic hydroxylation of TMB [10]



which, as the final result, with an unchanged rate of TMBQ decomposition, leads to an increase in the selectivity of the reaction with respect to the desired product.

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DECOMPOSITION OF H_2O_2 ON COPPER-CONTAINING ION-EXCHANGE RESINS OF THE VINYLPYRIDINE SERIES

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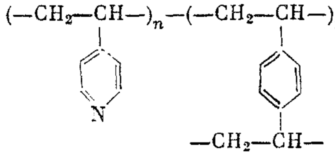
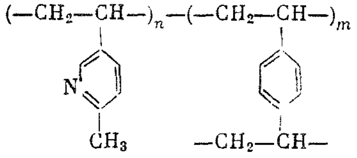
By means of kinetic studies and EPR, it has been shown that, in the reaction of hydrogen peroxide decomposition in the presence of copper-containing anion-exchange resins of the vinylpyridine series AN-40, AN-25, and AN-251, the catalytic activity increases in a series of complexes of the following types: $Cu(Py)_2{}^{2+} < Cu(Py)_3{}^{2+} < Cu(Py)_4{}^{2+}$. Increases in the degree of polymer cross-linking and increases in the content of copper complexes above 0.2 mg-ion/g lead to the appearance of steric hindrance to free diffusion of H_2O_2 molecules within the globules of resin, with a consequent decrease in specific catalytic activity of the ion-exchanger/metal complexes. It has been established by means of EPR and IR spectroscopy that in AN-25 and AN-251 CH_3 groups of the coordinated units are oxidized to carboxyl, with a consequent change in composition and structure of the Cu(II) complexes in the resins. Moreover, the copper ions are partly washed out from the resin into the reaction medium.

The decomposition of hydrogen peroxide in the presence of ion-exchanger/metal complexes (IMCs) has been investigated repeatedly [1-3]. However, the question of how the catalytic activity is related to the composition and structure of the coordination sphere and the spatial organization of the IMC has thus far been studied very little. Here we are reporting on an investigation of the reaction of H_2O_2 decomposition in the presence of complexes of Cu(II) with anion-exchange resins of the vinylpyridine series AN-40, AN-25, and AN-251.

EXPERIMENTAL

The anion-exchange gel resins AN-40, AN-25, and AN-251 have the following structures:


AN-40


AN-25, AN-251

The AN-251 is the macroporous analog of the AN-25 resin.

The degree of cross-linking in the various specimens, defined as the percentage of divinylbenzene (DVB) $\beta = 100\ m/(m + n)$ ranged from 4% to 20%. The procedure used in treating the resins to remove inorganic material and low molecular weight impurities is set forth in [4], as is the procedure for obtaining nonprotonated and partially protonated forms of the anion-exchange resins. The pH was measured in an LPU-01 potentiometer and a pH-262 instrument.

Complexes of Cu(II) with AN-40, AN-25, and AN-251 were obtained by treating the resins with aqueous solutions of copper nitrate (analytically pure grade) with various concentra-

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