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REACTION OF ORGANIC OXYGEN-CONTAINING COMPOUNDS WITH SOME HETEROPOLY COMPLEXES

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Under the influence of temperature, pressure, or irradiation heteropoly acids (HPA) and their salts enter into reaction with alcohols, ketones, and other organic reducing agents [1-3]. The change in the state of the HPA during reduction has been studied in a fair amount of detail, but data on the transformations of organic compounds during oxidation with HPAs are extremely limited. On the whole, the reaction of the organic compound with the HPA is determined by the oxidation–reduction, acid, and stereochemical characteristics of the reaction. The latter are exceptionally specific for heteropoly compounds (HPC) in connection with features of the structure of the metal–oxygen anion [4] and the possibility of the realization of reaction processes in the volume of the catalyst [5]. The relation between the catalytic reactions and reactions leading to the reduction of the heteropoly anion is at present the subject of an investigation [5]. The foregoing applies fully to one of the typical representatives of HPAs, i.e., silico-12-molybdic acid $H_4SiMo_{12}O_{40}$ (SMA). The high catalytic activity of SMA in the polycondensation of benzyl alcohol and the acylation and alkylation of aromatic compounds is well known [6, 7].

We have found that when anhydrous SMA is treated with the vapors of organic oxygen-containing compounds the acid is reduced stoichiometrically according to the equation:

$$H_4SiMo_{12}{}^{VI}O_{40} + n[H] \rightarrow H_4H_nSiMo_n{}^{V}Mo^{VI}_{12-n}O_{40}$$

where n = 2, 4 and depends on the nature of the reagent. The present work gives the results from an investigation into the products formed during the heterogeneous processes of oxidation of some organic substances at SMA.

EXPERIMENTAL

As reducing agents we used oxygen-containing compounds differing in the nature of the functional group (alcohols, aldehydes, ketones, carboxylic acids) and in the length of the carbon chain (1-3 atoms). All the reagents were of chemical purity or spectroscopic grades. The reaction of SMA with the organic compounds was realized at 170°C in a flow-type reactor connected to vacuum equipment. A 10-g sample of the SMA which had previously been purified by the etherate method and recrystallized was dehydrated in a drying cabinet at 160°C. The residual quantities of water were removed by holding at 170°C under vacuum. The degree of dehydration was determined by thermogravimetric analysis for water content. A sample of the SMA was then treated with vapor of the organic compound at 170°C for several hours. The flow rate of the vapor was determined by the conditions for evaporation of the reagent under vacuum and was not measured specially. The volatile products were collected in a receiver cooled with liquid nitrogen and investigated. In the case of methanol samples were taken periodically during the reaction and submitted to low-temperature fractional distillation to study their composition and to partial or complete separation. The reaction of SMA with ethanol was investigated in the

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range of 120-320°C. The composition of the mixture of substances formed in 1 h was investigated at five different temperatures.

A combination of mass spectrometry and IR and PMR spectroscopy was used to identify the organic products. The mass spectra were obtained on a "Varian MAT-311A" spectrometer under standard conditions with ionization by electron impact at 70 eV. In a number of cases exact measurement of the mass of the ions was used to determine the elemental composition. The IR spectra of the volatile products were recorded in gas cuvettes with a length of 10 cm on a "Specord 75-IR" spectrophotometer in the region of 4000-650 cm^{-1}. The PMR spectra were obtained on a "Tesla BS-467" high-resolution spectrometer at 60 MHz. Published data [8, 9] were used during the interpretation of the spectra.

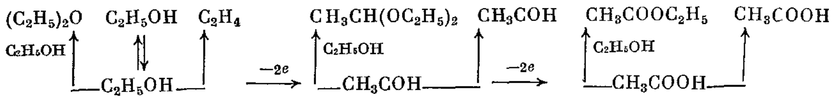
DISCUSSION OF RESULTS

Investigation of the IR spectra of the mixture of products from the reaction of SMA with methanol made it possible to record three groups of absorption bands, the intensity of which varied similarly in the various samples taken during the reaction. Each of them characterized an individual compound. Some of the products, possessing high volatility, were separated from the unreacted methanol by low-temperature fractional distillation. Two substances were isolated only at the initial stage of the reaction and were evidently the products from oxidation of methanol. One of them was characterized by absorption at 1750 ($C=O$) and 1207 cm^{-1} ($C-O$) and was identified as $HCOOCH_3$, while the other $CH_2(OCH_3)_2$ was recorded by absorption bands at 1148 and 936 cm^{-1} ($C-O$). The mass spectrum also contained peaks for methylal ions (m/z 45, 75) with considerable intensity. The third most volatile compound is formed from methanol throughout the whole reaction, and the intensity ratio of the lines for this product and methanol remained approximately constant during the reaction. Its IR spectrum corresponds to $(CH_3)_2O$.

In order to investigate the role of the Brönsted acidity in the reaction we studied the composition of the products from the reaction of methanol also with the potassium salts of SMA $K_4SiMo_{12}O_{40}$(K_4 SMA) at 270°C. At lower temperatures the processes involved in the reaction of methanol with the salt are hardly observed at all. The qualitative composition of the mixture as a whole corresponds to that given for SMA, but the formation of dimethyl ether occurs to a significantly lesser degree and stops completely when reduction is complete. Apart from this, at 270°C partial decomposition of the methyl formate into CH_4 and CO_2 occurs, and the IR spectrum contains their absorption lines. Thus, stoichiometric oxidation and catalytic dehydration of methanol is observed in the reaction of metanol with SMA and K_4SMA. The main difference lies in the incomparably higher activity of the acid, particularly in the catalytic dehydration reaction. The marked decrease in the catalytic activity of the heteropoly complex with gradual substitution of the SMA protons by the cation of the salt was also observed in [10].

Similar processes determine the reaction of SMA with ethanol at 170°C. The mixture of liquid products contained acetal, i. e., the homolog of methylal. In view of the identity of the types of fragmentation in these compounds the base peaks in the mass spectra of the products from the oxidation of the C_2H_5OH and CH_3OH differ by 28 m/z units (two CH_2 groups). During the dehydration of ethanol diethyl ether and ethylene are formed. The IR spectrum also contains bands for acetaldehyde. In the above-mentioned substances ethyl acetate and acetic acid were detected from the change in the form of the carbonyl vibration in the IR spectrum of the mixture during investigation of the temperature dependence of the qualitative composition of the reaction products. With increase in temperature the yield of diethyl ether passes through a maximum. The degree of conversion of the alcohol into ethylene increases, and at 270°C ethylene is the only product from dehydration, which goes almost to completion.

Thus, the results can be represented by the following scheme:



The products from successive oxidation of ethanol by SMA (acetaldehyde and acetic acid) were isolated in the form of the corresponding ethers or esters (acetal and ethyl acetate) or in the free state. The esters are formed preferentially at temperatures up to 220°C, whereas under the conditions for almost complete transformation of the ethanol into ethylene (270-320°C) the mixture only contains the aldehyde and acid. The amount of oxidation products formed is determined by the maximum degree of reduction of the SMA by the primary alcohol attainable at the given temperature (four at 170°C). The dehydration reactions are due to the

TABLE 1. The Products from Heterogeneous Reaction of the Vapor of the Investigated Organic Compounds with SMA

Reagent	Main reaction products	
	oxidation	dehydration, condensation
CH_3OH	$CH_2(OCH_3)_2$, $HCOOCH_3$	$(CH_3)_2O$
C_2H_5OH	$CH_3CH(OC_2H_5)_2$, CH_3COH, $CH_3COOC_2H_5$, CH_3COOH	$(C_2H_5)_2O$ C_2H_4
$(CH_3)_2CHOH$	$(CH_3)_2CO$	C_3H_6
HCOH	CO	
CH_3COH	CH_3COOH	Paraldehyde $C_6H_{12}O_3$
$(CH_3)_2CO$		$(CH_3)_2CCHCOCH_3$
HCOOH	CO_2	CO

catalytic action of the SMA protons. The last point is confirmed by the fact that the activity of SMA in dehydration reactions does not decrease during the reaction, while its potassium salt does not exhibit such activity at all.

It should be noted that the processes in the reaction of primary alcohols with SMA which we investigated and their catalytic oxidation in the presence of the oxides MoO_3, Cr_2O_3, V_2O_5 [11-14] lead to mixtures of products with similar composition. During investigation of the catalytic processes it was established that they are characterized by a "stage" mechanism, involving addition of the alcohol molecules to the catalyst, oxidation of the alcohol, isolation of the reaction products, and oxidation of the catalyst by oxygen [11-14]. It is supposed that the first stage of the process is "dissociative" addition of the alcohol to the metal–oxygen system, consisting of the formation of M–OH and M–OCH_2R groups (M = Mo, Cr, V). Hydride transfer of the hydrogen of the alkoxy group then takes place, and the oxidation product and, finally, water are isolated. The reaction takes place with the preferential formation of the free aldehyde or the acetal, depending on the nature of the oxide system, and its direction is determined by the bridge or terminal M–O bond to which the alcohol adds. The lability of the oxygen atoms of the oxide lattice, which are removed in the composition of water during the oxidation–reduction cycle, is considered to be an essential condition for catalytic activity.

The agreement in the composition of the products makes it possible to suppose that the main ideas about the mechanism of the catalytic reactions (dissociative addition, hydride transfer) can also be applied in our case. However, they are not in a state to explain the specific characteristics of the processes involving the HPA. We established that the results from the reduction of SMA by primary alcohols at 170°C is addition of "additional" protons by the acid and not removal of lattice oxygen, as in the case of oxides. Another important point is the fact that the protons of the acid inevitably play a definite role in the oxidation processes. This is indicated, in particular, by the fact that the potassium salt of SMA does not exhibit appreciable oxidative activity at $<$ 200°C, whereas the acid reacts at a lower temperature. The role of Brönsted acidity can evidently lie in the relatively stronger bonding of the alcohol by the heteropoly acid at the first stage of the reaction.

Replacement of the metal which forms the heteropoly anion leads to a different composition in the reaction products. The reaction of ethanol with anhydrous silico-12-tungstic acid $H_4SiW_{12}O_{40}$ (STA) was investigated. It has a higher proton-donating activity and lower oxidative capacity than SMA. The anions of SMA and STA are identically constructed in accordance with the Keggin structure. The reaction was realized at 350°C, since STA is thermally more stable than SMA and holds the solvated molecules more firmly. The reduction of STA was not detected during the reaction, like the oxidation of ethanol by STA. The mass spectra of the mixture contained strong peaks for the hydrocarbon ions $C_nH_{2n+2}^+$, $C_nH_{2n+1}^+$, $C_nH_{2n}^+$, and $C_nH_{2n-1}^{\cdot+}$. Data on the composition of the ions were obtained by exact measurement of the masses. It was established as a result that the ethanol is converted almost completely during reaction with STA into a mixture of olefins and alkanes C_nH_{2n} and C_nH_{2n+2} (n = 2-6). The formation of hydrocarbons with a chain length of 3 and 5 atoms in addition to ethylene in this case can only be explained on the assumption that the C–C bond of ethanol or its intermediate transformation products is broken and is most likely a secondary process.

According to the IR spectrum, isopropanol forms propylene C_3H_6 in reaction with SMA. The dehydration of isopropanol under these conditions is evidently catalyzed by the SMA protons. The oxidation of isopropanol occurs at the same time. Acetone was detected in the mixture of reaction products by mass spectrometry (molecular weight 58). In addition, weaker peaks with m/z 74, 32, 30 were recorded in the spectrum. The appearance of the last two peaks, corresponding to the CH_4O^+ and CH_2O^+ ions, can be explained if it is assumed that a compound containing the OCH_3 group, e.g., methyl acetate (molecular weight 74), is formed during more intensive oxidation of isopropanol associated with bond cleavage.

The oxidation product was not found during investigation of the reaction of SMA with acetone. The data from investigation of the solid phase indicate that stoichiometric oxidation–reduction processes occur. It can be supposed that at 170°C the oxidized form of acetone is firmly held by the SMA or decomposes. As in the case of isopropanol, the mass spectrum of the mixture contains a peak for the ion CH_3O^+ (m/z 31). The heterogeneous oxidation of acetone and acetaldehyde by SMA takes place in parallel with the condensation processes. In the case of acetone the main condensation product is mesityl oxide (molecular weight 98), which was identified by mass spectrometry. As known, mesityl oxide is also formed as a result of a homogeneous reaction catalyzed by acids. The mass spectrum of the products from the reaction of SMA with acetaldehyde indicates the formation of paraldehyde, i.e., the trimer of acetaldehyde. The PMR spectrum shows that about 90% of the aldehyde is trimerized during the reaction.

The oxidation of formaldehyde by SMA leads to the formation of CO and H_2O on account, possibly, of the instability of the HCOOH, which is oxidized to CO_2 and H_2O under the reaction conditions, and its decomposition to CO and H_2O clearly takes place at the same time. The results from investigation of the reaction of organic substances with SMA are given in Table 1.

CONCLUSIONS

1. At 170°C silico-12-molybdic acid (SMA) exhibits oxidative characteristics and simultaneous catalytic action in reactions with a series of organic oxygen-containing compounds. The oxidation of primary alcohols by SMA leads to a mixture of ethers, esters, and acetals. The formation of olefins, carboxylic acids, and aldehydes is also possible, and their yields increase with increase in temperature.

2. In the reaction of SMA with acetaldehyde and acetone condensation reactions also take place to a significant degree, in addition to the oxidation–reduction processes.

3. The SMA exhibits significantly higher activity than its neutral potassium salt both in stoichiometric oxidation reactions and in catalytic dehydration reactions. This is determined by the role of the Brönsted acidity of the heteropoly complex in the investigated processes.

4. The reaction of silico-12-tungstic acid with ethanol leads to a mixture of olefins and alkanes.

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