CONCLUSIONS

When heated, acetylene reacts with elemental sulfur in aqueous medium, in the presence of the $KOH-SnCl_2$ system, to give cis-1-vinylthio-1-buten-3-ol and cis,cis-di(3-hydroxy-1-butenyl) sulfide in a 4:1 ratio.

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CARBALKOXYLATION OF ACETYLENE IN SOLUTIONS OF MOLYBDENUM AND TUNGSTEN COMPLEXES

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The esters of the acrylic, propionic, succinic, maleic, fumaric, and other acids can be obtained by the carbalkoxylation of acetylene. The most active catalysts for this reaction are the Pd, Ni, and Co compounds [1, 2], although it is reported that the halides, sulfides, carbonyls, and other complexes of nearly all of the Group VIII metals are active.

Data on the participation of Mo and W compounds in this reaction are unknown to us, but the elements of the Cr subgroup form numerous complexes with CO and acetylene [3, 4]. In addition, Mo and W compounds catalyze the carbonylation of alcohols [5] and nitro compounds [6], and also the oxidative carbonylation of ethylene [7], reactions whose mechanism has much in common with the mechanism for the carbalkoxylation of acetylene [8]. In view of this it seemed of interest to study under mild conditions the catalytic activity of Mo and W compounds in the carbalkoxylation of acetylene.

EXPERIMENTAL

The nitrosyl carbonyl complexes were synthesized by known procedures: $C_5H_5(CO)_2MNO$ (M = Mo, W) [9], $C_5H_5(CO)(Ph_3P)\cdot WNO$ [10]. $HW_2(CO)_9No$ [11]. The substituted carbonyl halides of type $C_5H_5(CO)_2LMX$ (L = PPh_3, X = Cl, Br, M = Mo; L = $SbPh_3$, X = Cl, Br, I, M = Mo, W; L = $AsPh_3$, X = Cl, Br, M = Mo, W; X = Cl, M = Mo) were prepared by reacting $C_5H_5(CO)_3MX$ with 10-15% excess L under reflux in either benzene (M = Mo) or xylene (M = W). The complexes $C_5H_5\cdot(CO)_2LMoX$ (L = PPh_3, X = Cl, I; L = $SbPh_3$, $AsPh_3$, X = Cl, Br, I) and $C_5H_5(CO)_2LWCl$ (L = $AsPh_3$, $SbPh_3$) were previously obtained by the thermal reaction of $C_5H_5(CO)_3MX$ with L in benzene [12]. Replacing the benzene by xylene in the case of the W derivatives permits accelerating the reaction. The reaction time was checked by the disappearance of the ν_{CO} band of $C_5H_5\cdot(CO)_3MX$ and, as a rule, it was run for 1.5-3 h. The $C_5H_5(CO)_2LMX$ complexes were recrystallized either from 1:2 chloroform—heptane or toluene—heptane mixtures, or they were chromatographed on Al_2O_3 using benzene as the eluant. In those cases (X = Br, I) where the reaction products represent a mixture of the cis and trans isomers [13, 14] the isomers were not isolated in the pure state.

The experiments on testing the catalytic activity were run in a gas-flow reactor with complete mixing, at 70°C, 0.1 MPa, CO/C_2H_2 ratio = 1, and [HCl] = 0.1-0.5 mole/liter, in n-butanol solution. Depending on the solubility in n-BuOH, the concentration of the studied complexes ranged from 0.025 to 0.1 mole/liter. In individual cases, to increase the solubility of the W and Mo compounds, 1 ml of DMF was added to 3 ml of n-BuOH (usual volume of the solution). The need of adding HCl is due to the fact that hydrogen halides (HCl, HBr,

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TABLE 1

Complex	Average rate of forming products, mole/liter·h·10^2		
	n-Butyl acrylate	Di-n-butyl succinate	n-Butyl propionate
$CpMo(CO)_2NO$ (I)	0,69	0,18	0,31
$CuMo(CO)_2(PPh_3)Cl$ (II)	0,61	–	0,21
$CpMo(NO)(PPh_3)(SnBr_3)Br$ (III)	0,30	–	0,30
$CpW(CO)_2(NO)$ (IV)	0,41	–	Traces
$CpW(CO)(NO)(PPh_3)$ (V)	0,62	–	0,32
$HW_2(CO)_9(NO)$ (VI)	0,51	–	0,41

Cp = cyclopentadienyl.

HI) facilitate an increase in the stability and activity of catalytic carbonylation systems. The time of the experiments was 2-3 h. The composition of the contact solution was determined by GLC at the end of experiment.

The following complexes were studied by the described method: $CpW(CO)(NO)PPh_3$, $HW_2 \cdot (CO)_9(NO)$, $CpMo(NO)PPh_3(SnBr_3)Br$, $CpM(CO)_2(NO)$ (M = Mo, W), $CpM(CO)_2LX$, where when L = PPh_3, X = Cl, Br, M = Mo. When L = $SbPh_3$X = Cl, Br, I; M = Mo, W. When L = $AsPh_3$, X = Br, I; M = Mo, W; X = Cl; M = Mo.

DISCUSSION OF RESULTS

Most of the complexes lacked catalytic activity. However, in the case of compounds (I)-(VI) (Table 1) we recorded the formation of butyl acrylate and butyl propionate, and in the presence of (I) also of dibutyl succinate. The rate of forming the products is ~100 times slower than in the PdI_2—LiI—HCl system under comparable conditions [15]. However, the very fact of forming the carbalkoxylation products of acetylene with the involvement of Mo and W compounds under very mild conditions (0.1 MPa, 70°) seems quite interesting. In contrast to the described catalytic systems, such oxidative carbalkoxylation products of acetylene as the maleate, fumarate, and muconate are not formed in solutions of the investigated Mo and W complexes. The formation of butyl propionate can be related to the reduction of the acrylate by the complexes in the presence of HCl. It is interesting to mention the very high selectivity of the $CpW(CO)_2(NO)$ complex, which catalyzes the exclusive formation of n-butyl acrylate.

The obtained results permit expanding the scope of the search for acetylene carbonylation catalysts and create prerequisites for creating new promising processes for the synthesis of monomers and organic synthesis intermediates.

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CONCLUSIONS

The carbonyl nitrosyl and carbonyl halide complexes of Mo and W catalyze the carbalkoxylation of acetylene to give predominantly n-butyl acrylate and n-butyl propionate.

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