ORGANIC CHEMISTRY

OXIDATIVE CARBONYLATION OF ORGANIC COMPOUNDS BY CARBON MONOXIDE AND TRANSITION-METAL SALT CATALYSTS

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Oxidative carbonylation of organic compounds in the presence of O_2 or air is an appropriate method for obtaining a wide range of chemical substances. From ethylene under CO and O_2 pressure at 100-125°C, acetic acid and acetic anhydride are obtained from the reaction mixture, whereas in the presence of $PdCl_2$ acrylic acid is formed [1, 2]. Likewise, salts of Re, Be, Mn, Ti, and W [3] have been employed. To the reaction medium, salts of Cu(II) or Fe(III) have been generally added, and on some occasions LiCl. During the oxidative carbonylation of alcohols in the presence of $PdCl_2$—$CuCl_2$, dialkyl oxalates together with dialkyl carbonates [4] are formed. The activity and selectivity of the catalytic systems of oxidative carbonylation of olefins and alcohols have been insufficiently studied.

The goal of the present work is to study the catalytic properties of catalytic systems incorporating salts of transition metals in the carbonylation of ethylene and methanol.

EXPERIMENTAL

The experiments were performed in a glass-lined steel revolving autoclave of 0.15-liter capacity. The autoclave was charged with 0.5 g $PdCl_2$, 2.5 g $CuCl_2$, 2.5 g LiCl, and 50 ml solvent. Ethylene and CO were introduced from cylinders. The reaction was carried out at 125° under combined C_2H_4 and Co pressure of 60-100 atm. Air was fed into the autoclave to make the O_2 pressure 4.6-5.7 or 25.5 atm. The solvents used were distilled CH_3OH, n-hexane, tetrahydrofuran (THF), and pyridine of about 99.9% purity. In experiments with CH_3OH the autoclave was charged with 0.5 g $MnCl_2$, 2.5 g $CuCl_2$, 2.5 g LiCl, and 19.8 g CH_3OH. Carbon monoxide up to a pressure of 40-50 atm was introduced followed by air up to a pressure of 160 atm (22.5 atm O_2). The autoclave was then heated to 140-180°. At the completion of the experiment (5 h) the products were distilled and analyzed on an LKhM-8MD chromatograph with a flame-ionization detector (2-m column of 15% polyethylene glycol succinate on Chromosorb W, 60-80 mesh, gas flow 30 ml/min). The products of the reaction were separated on a preparative chromatograph LKhP-5A with an 8 × 10 mm steel column of 20% polyethylene glycol on Chromosorb P, carrier gas N_2, prior to the determination of the physical constants of methyl acrylate (d_4^{20} 0.9572; n_D^{20} 1.4032) and of dimethyl carbonate (d_4^{20} 1.0681; n_D^{20} 1.3687). The yield of methyl acrylate (MA) was based on the initial ethylene present, and the yields of methyl acetate (MAc) and dimethyl carbonate (DMC) were based on added CH_3OH.

DISCUSSION OF RESULTS

The oxidative carbonylation of ethylene under partial oxygen pressure (p_{O_2}) 4.6-5.7 atm and in the presence of either aqueous or nonaqueous $PdCl_2$ practically did not proceed (Table 1). The yield of MA was only 1-2%. The addition of LiCl increased the yield of MA insignificantly. The simultaneous presence in the system of $CuCl_2$ and LiCl resulted in an increase of MA yield of 15-17% and of MAc by 14-16%. In the presence of $PdCl_2$ + LiCl or $PdCl_2$ + $CuCl_2$ the reaction proceeded proportionally to the catalyst stoichiometry. Upon the addition of LiCl to the $PdCl_2$ + $CuCl_2$ system, the yield of MA was 10 moles per mole $PdCl_2$, proof of the catalytic nature of the reaction. At p_{O_2} 22.5 atm in the presence of $PdCl_2$ and $CuCl_2$ but not LiCl, the yield of MA was small, but in basic solution methyl propionate (up to 32%) was

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TABLE 1. Oxidative Carbonylation of Ethylene in the Presence of $PdCl_2$–$CuCl_2$–LiCl and CH_3OH at 125°C

Catalytic system	Component weight ratio	Initial pressure, atm			Reaction product yields, %	
		C_2H_4	CO	O_2	MA based on initial ethylene	MAc based on initial methanol
$PdCl_2$–$CuCl_2$	0,5:2,5	40	60	4,6	2,2	0,0
$PdCl_2$–$CuCl_2 \cdot 2H_2O$	0,5:2,5	40	60	4,6	1,0	0,0
$PdCl_2$–LiCl	0,5:2,5	40	50	5,7	4,6	0,4
$PdCl_2$–$CuCl_2$–LiCl	0,5:2,5:2,5	40	50	5,7	17,3	15,8
The same	0,5:2,5:2,5	40	50	4,6	15,7	13,7
" "	0,5:2,5:2,5	40	60	4,6	15,3	4,6
$PdCl_2$–$CuCl_2$	0,5:2,5	30	30	22,5	1,4*	6,6
$PdCl_2$–$CuCl_2$–LiCl	0,5:2,5:2,5	40	50	22,5	70,2	10,5
The same	0,5:2,5:2,5	30	40	22,5	73,0	22,6
" "†	0,5:2,5:2,5	30	40	22,5	68,0	18,0
" "‡	0,5:2,5:2,5	30	40	22,5	53,0	1,7
" "**	0,5:2,5:2,5	30	40	22,5	28,0	2,1

*Formation of methyl propionate, 32.2%.
†THF solvent.
‡Pyridine solvent.
**Hexane solvent.

TABLE 2. Oxidative Carbonylation of Methanol in the Presence of $MnCl_2$–$CuCl_2$–LiCl Catalytic System

Initial O_2 pressure 22.5 atm, CO 40 atm, 140°C

Catalytic system	Catalyst component weight ratio	Methanol conversion, %	Reaction product yields based on methanol, %	
			dimethyl carbonate	methyl acetate
LiCl*		0,0	0,0	0,0
$MnCl_2$*		18,0	8,0	6,0
$CuCl_2$*		18,0	10,0	1,3
$CuCl_2$–LiCl	1:1	30,8	6,5	15,0
$MnCl_2$–$CuCl_2$–LiCl	0,5:2,5:2,5	56,0	20,7	18,7
$MnCl_2$–$CuCl_2$–LiCl	0,5:2,5:2,5†	57,7	23,0	5,2
$MnCl_2$–$CuCl_2$–LiCl	0,5:2,5:2,5‡	96,0	89,0	5,7

*Amount of catalyst 2.5 g.
†Initial CO pressure 50 atm.
‡180°C.

formed. Addition of LiCl to the catalyst system altered the course of the reaction, and MA in 70-73% yield was formed.

Investigations on the effect of solvents on the carbonylation reaction showed that THF had no effect on the formation of MA, but the presence of pyridine and n-hexane lowered the yields of MA and MAc. In THF and pyridine a significant amount of tarry products was formed. In this manner CH_3OH, serving also as reagent, was most effective as solvent. In all experiments a small amount (up to 10%) of CO_2 was formed, apparently as a result of CO oxidation. Oxidative carbonylation in the presence of O_2 and analogous catalytic systems generally results in the formation of significant amounts of β-methoxypropionic acid or its ester [2]. Using air we were able to increase the reaction selectivity with respect to MA formation. The infrared spectrum of the isolated product had absorption bands at 850, 1000, 1070, 1200, 1277, 1400, 1440, 1620, 1640, 1740, 2960, and 3000 cm^{-1}, which corresponded with the reported infrared spectrum of MA [5].

Methyl alcohol in the presence of LiCl and $MnCl_2$ (Table 2) barely reacted with CO. The carbonylation of CH_3OH was catalyzed by $CuCl_2$, but the yield of DMC did not exceed 10%, which was in accord with previous work [5]. The addition of $MnCl_2$ and LiCl to $CuCl_2$ increased the yield of DMC twofold (20.7%) and barely changed with increase of CO pressure. However, the yield of MAc decreased under this condition. Increasing the temperature from 140° to 180° increased the yield of DMC to 89% and decreased the MA yield. In all experiments on the oxidative carbonylation of CH_3OH, the pressure decreased after 4 h. In the experiment conducted at 180°, pressure decrease was observed for 10 h. In the infrared spectrum of isolated DMC, absorption was detected at 800, 920, 1280, 1460, 1750, 2860, 2960, and 3010 cm^{-1}, corresponding to that reported [5]. In the NMR spectrum of DMC there was a signal at 3.74 ppm corresponding to the OCH_3 group.

CONCLUSIONS

1. The yield of methyl acrylate during oxidative carbonylation of ethylene in the presence of chlorides of palladium and copper sharply increased with the addition of LiCl and during the increase of the partial pressure of carbon monoxide in the gaseous mixture.

2. Highly effective as a catalyst, methanol served simultaneously as the reagent and formed methyl acrylate in yields approaching 73%.

3. In oxidative carbonylation of methanol, the system $MnCl_2$—$CuCl_2$—LiCl was highly active. At 180°, 40 atm carbon monoxide pressure, and 22.5 atm oxygen the yield of dimethyl carbonate approached 89%.

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NICKEL-COMPLEX-CATALYZED ADDITION OF METHANOL TO ESTERS OF α,β-UNSATURATED ACIDS

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Alcohols add to esters of α,β-unsaturated acids in the presence of strongly alkaline reagents and an excess of the alcohol [1, 2]. Information is lacking regarding the catalysis of these reactions by complexes of the transition metals.

We studied the addition of methanol to methyl acrylate (MA), methyl methacrylate (MMA), dimethyl maleate (DMM), and dimethyl fumarate (DMF) in the presence of nickel complexes. The methyl ester of β-methoxypropionic acid (I) was produced in approximately 100% yield when a 1:1 mixture of methanol and MA were reacted in a diethyl ether solution of $Ni(acac)_2$,

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