Carbonylation of acetaldehyde in the presence of transition metal compounds

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The carbonylation of acetaldehyde to give butyl lactate has been carried out in the presence of rhodium and cobalt compounds at P_{CO} = 5—9 MPa and T = 383—483 K.

Key words: acetaldehyde, carbonylation, Co, Pd, Rh compounds.

Lactic acid and its esters (lactates) are valuable organic compounds that can be obtained by carbonylation of acetaldehyde

$CH_3CHO + CO + 2ROH \rightarrow CH_3CH(OR)C(O)OR + H_2O$,
where R = H, Alk.

Only a few examples of this reaction in the presence of acid catalysts under rigorous conditions (35—45 MPa) are known.[1—4]

We attempted to carry out carbonylation of acetaldehyde in the presence of Group VIII transition metal compounds. By analogy with the carbonylation of olefins,[5] one might expect that the replacement of acid catalysts by transition metal compounds would allow carbonylation of acetaldehyde to occur under milder conditions. The activities of a series of Pd, Co, and Rh compounds in this reaction carried out at P_{CO} = 5—9 MPa and T = 383—483 K were studied for R = C_4H_9. The results obtained are listed in Table 1.

The Pd compounds were inactive under the conditions studied. Cobalt was active only when it was used as the carbonyl, $Co_2(CO)_8$. The modification of the latter with phosphines (PPh_3 and PBu_3) increased its activity. Rh in the form of its carbonyl exhibited no noticeable activity, but it catalyzed the reaction when used as $RhCl_3$. In the presence of CH_3I or phosphines (PPh_3 and PBu_3), the activity decreased, and in the presence of HI it increased. The best result was achieved when the $Co_2(CO)_8$—$RhCl_3$ bimetallic catalytic system with a Co/Rh atomic ratio of 4 was used.

The activity of catalytic systems based on Co and Rh increased 10-fold as the CO pressure increased from 5 to 9 MPa and did not depend on the temperature over the 383—483 K temperature range.

Unlike Co and Rh compounds, acids did not catalyze carbonylation of acetaldehyde under the conditions considered.

Table 1. The results of carbonylation of acetaldehyde to give butyl 2-butoxypropionate (dibutyl lactate, DBL) in the presence of transition metal compounds (T = 423 K, P_{CO} = 9 MPa, τ = 3 h)

Catalyst	Additive*	DBL (%)	$\frac{m^{**}}{h^{-1}}$
$PdCl_2$	—	0.0	0.0
	PPh_3	0.0	0.0
$CoCl_2$	—	0.0	0.0
$Co(CH_3COO)_2$	—	0.0	0.0
$Co_2(CO)_8$	—	4.0	0.8
	PBu_3	8.0	1.6
	PPh_3	7.0	1.4
$Rh_4(CO)_{12}$	—	0.0	0.0
	HI	0.0	0.0
$RhCl_3$	—	2.0	0.4
	PPh_3	0.0	0.0
	CH_3I	0.5	0.1
	HI	10.0	2.0
$RhCl_3+Co_2(CO)_8$	—	15.0	3.0
—	HI	0.0	0.0
—	HCl	0.0	0.0

* The P/M ratio was 10 g-at/g-at (M = Pd, Co, Rh); [HI], [CH_3I], [HCl] = 0.1 mol L^{-1}.
** m is the number of working cycles of the catalyst.

Experimental

Carbonylation of acetaldehyde was carried out at a constant pressure and a constant temperature in a 250 mL stainless-steel autoclave equipped with a stirrer. *n*-Butanol (40 mL) and a catalyst ($1.2 \cdot 10^{-4}$ mol) was placed in the autoclave, and then CO was pumped in until the working pressure was achieved. The resulting mixture was heated to a definite temperature, and then acetaldehyde (5.8 mL) was injected using a dosing apparatus. The reaction was carried out for 3 h.

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The liquid products were analyzed by GLC using a 3 m×2 mm column packed with N-*AW* Chromaton with 5 % PEG. Butyl 2-butoxypropionate (dibutyl lactate) was identified by GC-MS.

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