

## Carbonylation of acetaldehyde in the presence of transition metal compounds

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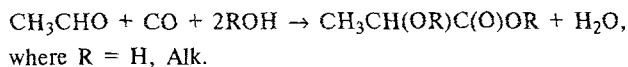
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The carbonylation of acetaldehyde to give butyl lactate has been carried out in the presence of rhodium and cobalt compounds at  $P_{\text{CO}} = 5\text{--}9$  MPa and  $T = 383\text{--}483$  K.

**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



Only a few examples of this reaction in the presence of acid catalysts under rigorous conditions (35–45 MPa) are known.<sup>1–4</sup>

We attempted to carry out carbonylation of acetaldehyde in the presence of Group VIII transition metal compounds. By analogy with the carbonylation of olefins,<sup>5</sup> 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  $P_{\text{CO}} = 5\text{--}9$  MPa and  $T = 383\text{--}483$  K were studied for R = C<sub>4</sub>H<sub>9</sub>. 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<sub>2</sub>(CO)<sub>8</sub>. The modification of the latter with phosphines (PPh<sub>3</sub> and PBu<sub>3</sub>) increased its activity. Rh in the form of its carbonyl exhibited no noticeable activity, but it catalyzed the reaction when used as RhCl<sub>3</sub>. In the presence of CH<sub>3</sub>I or phosphines (PPh<sub>3</sub> and PBu<sub>3</sub>), the activity decreased, and in the presence of HI it increased. The best result was achieved when the Co<sub>2</sub>(CO)<sub>8</sub>–RhCl<sub>3</sub> 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,  $P_{\text{CO}} = 9$  MPa,  $\tau = 3$  h)

Catalyst	Additive*	DBL (%)	$\frac{m^{**}}{\text{h}^{-1}}$
PdCl <sub>2</sub>	—	0.0	0.0
	PPh <sub>3</sub>	0.0	0.0
CoCl <sub>2</sub>	—	0.0	0.0
Co(CH <sub>3</sub> COO) <sub>2</sub>	—	0.0	0.0
Co <sub>2</sub> (CO) <sub>8</sub>	—	4.0	0.8
	PBu <sub>3</sub>	8.0	1.6
	PPh <sub>3</sub>	7.0	1.4
Rh <sub>4</sub> (CO) <sub>12</sub>	—	0.0	0.0
	HI	0.0	0.0
RhCl <sub>3</sub>	—	2.0	0.4
	PPh <sub>3</sub>	0.0	0.0
	CH <sub>3</sub> I	0.5	0.1
	HI	10.0	2.0
RhCl <sub>3</sub> +Co <sub>2</sub> (CO) <sub>8</sub>	—	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<sub>3</sub>I], [HCl] = 0.1 mol L<sup>-1</sup>.

\*\*  $m$  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.

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.

### References

1. S. K. Bhattacharyya, S. K. Palit, and A. R. Das, *Ind. Eng. Chem. Prod. Res. Develop.*, 1970, **9**, 92.
2. Jpn. Pat. 82106503; *Chem. Abstr.*, 1982, **97**, 162396p.
3. US Pat. 3948986; *Chem. Abstr.*, 1976, **85**, 5198.
4. A. L. Lapidus, S. Ya. Grobovenko, A. V. Goryachevskaya, and A. D. Kagarlitskii, *Izv. Akad. Nauk SSSR, Ser. khim.*, 1985, 1687 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 1546 (Engl. Transl.)].
5. R. A. Sheldon, *Khimicheskie produkty na osnove sintez-gaza*, Khimiya, Moscow, 1987 (Russ. Transl) [*Chemicals from Synthesis Gas*, D. I. Reidel Publishing Company, Dordrecht, Boston, Lancaster].

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