Table 1. Hydromenthoxycarbonylation of isobutylene with carbon monoxide and 1-menthol in the presence of the $Pd(acac)_2$–PPh_3–TsOH system. Molar ratio [1-menthol] : [isobutylene] : [$Pd(acac)_2$] = 435 : 550 : 1. Amount of $Pd(acac)_2$ is 0.035 g (0.115 mmol)

No.	Molar ratio of the catalyst components to $Pd(acac)_2$		Reaction conditions			Unreacted 1-menthol, % of initial quantity	Yield of 1-menthylisovalerate, %	
	[PPh_3]	[TsOH]	T, °C	Pco, MPa	τ, h		on fed 1-menthol basis	on reacted 1-menthol basis
1	2	12	100	2	4	79.8	13.2	65.3
2	3	12	100	2	4	74.2	19.3	74.8
3	5	12	100	2	4	75.1	21.5	90.1
4	7	12	100	2	4	28.3	67.6	94.3
5	9	12	100	2	4	44.2	48.2	86.4
6	7	8	100	2	4	56.6	35.3	80.5
7	7	10	100	2	4	26.6	61.9	84.1
8	7	13	100	2	4	53.5	36.7	80.1
9	7	12	90	2	4	40.6	54.8	91.8
10	7	12	110	2	4	40.1	52.1	87.3
11	7	12	100	1.5	4	46.5	46.9	87.2
12	7	12	100	2.5	4	57.9	39.7	97.1
13	7	12	100	2	2	54.2	39.2	85.6
14	7	12	100	2	5	62.0	30.2	79.8

99.8% purity, and *l*-menthol of 99.7% purity were used. The experiments were carried out in the solvent-free mode in a laboratory stainless steel autoclave unit. The components of the catalytic system and corresponding alcohols (ethanol, *l*-menthol) were loaded into an autoclave with a 100-ml capacity; the autoclave was sealed, purged with carbon monoxide, and charged with isobutylene and carbon monoxide; then, stirring and heating were switched on. After the completion of the reaction, the autoclave was cooled to ambient temperature, the pressure in the autoclave was reduced to atmospheric pressure, and the products were isolated by rectification according to the procedures described earlier [6, 10, 12]. The determination of the purity and the analysis of the products were carried out by means of a GLC technique on an LKhM-72 chromatograph with a thermal conductivity detector; stainless steel chromatographic columns 2-m-long and 3 mm in diameter packed with 5% Reoplex-400 on Chezasorb AW sorbent with a particle size of 0.15–0.25 mm. The temperature of the column oven was 110°C, that of the evaporator was 165–180°C, and the carrier gas (helium) flow rate was 30 ml/min.

RESULTS AND DISCUSSION

The influence of the various conditions of running the reaction of isobutylene hydromenthoxycarbonylation with carbon monoxide and *l*-menthol on the product yield was studied. The results are presented in Table 1. The carbonylation of isobutylene proceeds regioselectively at the terminal carbon atom yielding the linear product *l*-menthyl isovalerate. The reaction was carried out at a molar ratio of [*l*-menthol] : [*iso*C_4H_8] : [$Pd(Acac)_2$] = 435 : 550 : 1. As is seen from the data in Table 1, the reaction goes to completion in none of the runs: the recovery of unreacted *l*-menthol is 26.6–79.0% of the initial quantity.

The ratio of the components of the catalytic system has a strong effect on the yield of the product. An increase in the $PPh_3/Pd(Acac)_2$ ratio from 2 up to 7 results in an increase in the yield of *l*-menthylisovalerate from 13.2 up to 67.6% (Table 1, entries 1–4). The further increase in the excess of PPh_3 reduces the yield of the product (Table 1, entry 5). The increase in the $TsOH/Pd(Acac)_2$ ratio from 8 up to 12 increases the yield of the product from 35.3 up to 67.6% (Table 1; entries 4, 6, and 7). The optimum ratio of the components of the catalytic system turned out to be [$Pd(Acac)_2$] : [PPh_3] : [TsOH] = 1 : 7 : 12. Such an effect of the increase in the excess of triphenylphosphine and *p*-toluenesulfonic acid in the system on the yield of the product may apparently be explained by their stabilizing effect on the catalyst. The temperature, carbon monoxide pressure, and the reaction time also strongly affect the yield of the product. With an increase in the reaction temperature from 90 up to 100°C, the yield of the product increases from 54.8 to 67.6% (Table 1; entries 4 and 9). With the further increase in the temperature (Table 1, entry 10), a decrease in the yield is observed because of the catalyst deactivation (appearance of palladium black). The