

Hydroesterification of *tert*-butyl alcohol in room temperature ionic liquids

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Received (in Montpellier, France) 30th October 2001, Accepted 8th January 2002

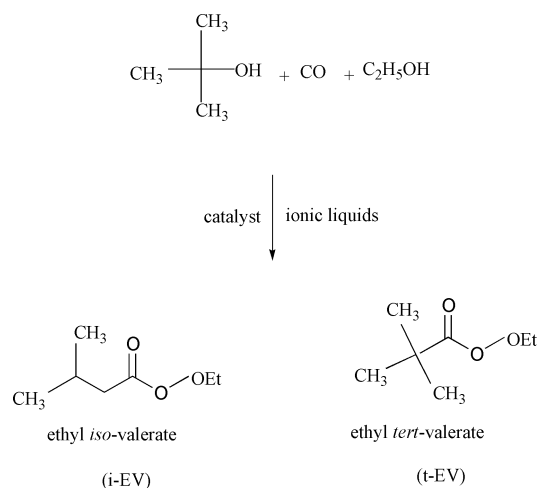
First published as an Advance Article on the web

Hydroesterification of *tert*-butyl alcohol with ethanol catalyzed by transition metal triphenylphosphine complexes in the presence of *p*-toluenesulfonic acid was investigated using room temperature ionic liquids as the reaction medium at 373–413 K and 3–6 MPa of CO. In comparison with the organic solvents as reaction medium, higher conversion was achieved and ethyl *tert*-valerate could be directly formed in the ionic liquid medium. The products could be separated from the ionic liquids easily due to their immiscibility in this medium.

Pivalic acid, 2,2-dimethylpropanoic acid, is one of the most important *tert*-carboxylic acids, being widely used as a starting material for various agrochemicals, pharmaceuticals, aroma chemicals, specialty chemicals and polymer additives.¹ Typically, pivalic acid is manufactured on the industry scale by non-catalytic Koch carbonylation of *iso*-butylene or *tert*-butyl alcohol with CO in strong acid medium, such as concentrated H₂SO₄, HF or BF₃ under high CO pressure.^{2,3} The amount of acid medium used for the reaction is usually equal or even greater than that of *iso*-butylene or *tert*-butyl alcohol, resulting in serious corrosion of equipment, difficulties in product separation and formation of a large amount of acidic waste water.⁴ Catalytic processes that involved using Cu⁺, Ag⁺ and Pd²⁺ as catalysts were conducted under relatively moderate reaction conditions,⁵ but strong inorganic liquid acid medium was also inevitably employed and the above disadvantages still remained. In view of the increasing emphasis on the adoption of clean manufacturing processes, environmentally benign, simple and efficient catalytic technologies for chemical production are highly desirable. For example, solid acids as catalysts for Koch carbonylation have recently been reported⁶ and to develop other novel environmentally friendly methods for manufacturing pivalic acid is of great significance.

At the same time, room temperature ionic liquids, as novel environmentally friendly solvents and catalysts, have received increasing recognition and acceptance.^{7–9} Many important organic reactions, including alkylation,¹⁰ cycloaddition,¹¹ hydrogenation,¹² esterification,¹³ Beckmann rearrangement,¹⁴ cyclodimerization¹⁵ and arylation,¹⁶ etc., have been reported to proceed in room temperature ionic liquids with excellent yields and selectivity, showing the great potential of ionic liquids in catalytic technologies for chemical production.

Hydroesterification of *tert*-butyl alcohol with CO catalyzed by Pd complexes in the presence of *p*-toluenesulfonic acid (*p*-Ts) in organic solvents had been reported previously, with the sole formation of *iso*-valerate.¹⁷ Formation of *tert*-valerate was not observed. In this work, the hydroesterification of *tert*-butyl alcohol with ethanol, using room temperature ionic liquids as the reaction medium and catalyzed by transition metal triphenylphosphine complexes in the presence of *p*-Ts, was performed for the first time and direct formation of ethyl *tert*-valerate was observed in this case [eqn. (1)].



Since ethyl *tert*-valerate is immiscible with ionic liquids, it is easy to recover it from the ionic liquid reaction system, and pivalic acid can be easily produced by hydrolysis of ethyl *tert*-valerate.

In comparison with organic solvents as reaction medium, the following advantages are achieved: (1) higher conversion, (2) easy recovery of the product, and (3) direct formation of ethyl *tert*-valerate.

Experimental

Preparation of transition metal triphenylphosphine complexes and room temperature ionic liquids

Preparation of Pt, Pd, Au, Co, Cu and Ru triphenylphosphine complexes can be found in the literature,^{18,19} and the following ionic liquids: butylpyridinium nitrate (Bpy[NO₃]), 1-methyl-3-butylimidazolium hexafluorophosphate (MBIm[PF₆]), 1-methyl-3-butylimidazolium nitrate (MBIm[NO₃]), 1-methyl-3-propylimidazolium tetrafluoroborate (MPIm[BF₄]), 1-methyl-3-ethylimidazolium tetrafluoroborate (MEIm[BF₄]) and 1-methyl-3-butylimidazolium tetrafluoroborate (MBIm[BF₄]), were synthesized according to previous reports.^{20,21} The only

Table 1 Results of hydroesterification of *tert*-butyl alcohol in different transition metal complex + ionic liquid + *p*-Ts catalyst systems^a

Entry	Catalyst	Reaction medium	Conv. (%)	Selectivity (%)				
				<i>i</i> -BE	ETBE	<i>t</i> -EV	<i>i</i> -EV	Dimer
1	Au(PPh ₃)Cl	MBIm[BF ₄]	68.9	24.9	75.1	—	—	—
2	Co(PPh ₃) ₂ Cl ₂	MBIm[BF ₄]	63.0	30.7	69.3	—	—	—
3	Cu(PPh ₃) ₂ Cl ₂	MBIm[BF ₄]	67.1	44.1	55.9	—	—	—
4	Pt(PPh ₃) ₂ Cl ₂	MBIm[BF ₄]	72.8	27.4	59.7	—	—	12.8
5	Ru(PPh ₃) ₄ Cl ₂	MBIm[BF ₄]	66.9	15.3	57.6	4.4	22.6	—
6	Ru(PPh ₃) ₃ Cl ₂	MBIm[BF ₄]	59.5	19.2	75.3	1.6	3.9	—
7 ^b	Pd(PPh ₃) ₂ Cl ₂	MBIm[BF ₄]	90.5	7.1	14.1	14.1	64.6	—
8	Pd(PPh ₃) ₂ Cl ₂	BPy[NO ₃]	84.3	11.3	19.2	14.7	54.8	—
9	Pd(PPh ₃) ₂ Cl ₂	MBIm[NO ₃]	89.1	8.1	13.8	15.6	62.5	—
10	Pd(PPh ₃) ₂ Cl ₂	MPIm[BF ₄]	89.7	5.2	14.9	14.2	65.1	—
11	Pd(PPh ₃) ₂ Cl ₂	MEIm[BF ₄]	90.1	6.2	13.2	14.9	65.7	—
12	Pd(PPh ₃) ₂ Cl ₂	MBIm[PF ₆]	88.5	10.8	24.1	8.2	30.1	26.7
13	Pd(PPh ₃) ₂ Cl ₂	Ethanol	73.6	13.4	48.6	—	38.0	—
14	Pd(PPh ₃) ₂ Cl ₂	Toluene	64.4	22.1	61.8	—	16.1	—

^a Reaction conditions: 6.0 MPa CO, 393 K, 12 h, catalyst: 0.084 mmol, *p*-Ts: 8.4 mmol, *tert*-butyl alcohol: 0.017 mol. ^b Isolated yield (*t*-EV + *i*-EV) is 60.1% with 96% in purity.

slight modification during preparation is that CHCl₃ was used as the extraction solvent instead of CH₂Cl₂, since it was found that slightly high yields for BF₄⁻ containing ionic liquids could be achieved with CHCl₃.

Reaction and analysis

For each reaction, 0.017 mol (*ca.* 1.6 ml) *tert*-butyl alcohol, 0.034 mol (*ca.* 1.9 ml) ethanol, 2 ml ionic liquid, 0.0033 to 0.012 mol *p*-toluenesulfonic acid (*p*-Ts) and 0.17 to 0.017 mmol transition metal complex catalyst were charged successively into a 90 ml stainless steel autoclave with magnetic stirring. After the reactor was purged 3 times with N₂, CO (99.9% purity, 3–6 MPa) was introduced at room temperature. The reactions proceeded at 100–140 °C for 6–24 h. After reaction and at room temperature, a liquid mixture with two phases was formed. The lower layer was the ionic liquid phase and the upper layer was the reaction mixture.

Although the desired products were almost entirely contained in the upper layer and quotation of isolated yields would be better, the following two reasons make us believe that it is better to quote conversion of *tert*-butyl alcohol and product selectivities: (1) 4–5 kinds of products were detected in the reaction mixture, with a distribution equilibrium of *tert*-butyl alcohol and its products between the upper reaction mixture phase and the ionic liquid phase, especially *tert*-butyl alcohol and by-products, which are miscible with ionic liquids and (2) quoting conversion of *tert*-butyl alcohol and product selectivities will clearly show the relationship between every product. Therefore, the two-phase mixture was homogenized by adding extra ethanol (*ca.* 2 ml) before analysis so as to acquire the concentration data of remaining reactant and products precisely.

Analysis was conducted with an Hewlett-Packard 6890 gas chromatograph/5973 mass spectrum instrument equipped with an HP 5MS column (30 m × 0.25 mm × 0.25 μm). The concentrations of reactant and products were directly given by the GC/MS Chemstation according to the area of each chromatograph peak.

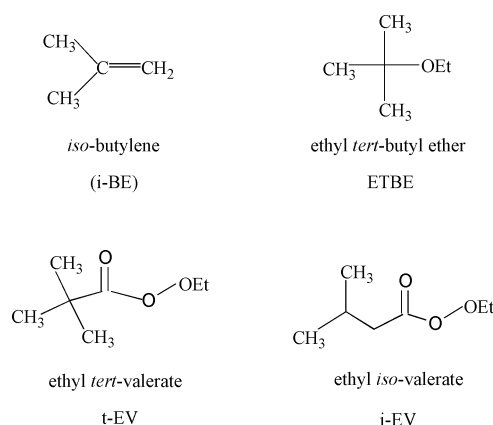
Results and discussion

Effect of transition metal complexes and ionic liquids on the hydroesterification of *tert*-butyl alcohol

The results of hydroesterification of *tert*-butyl alcohol with ethanol, catalyzed by a series of transition metal

triphenylphosphine complex catalysts in different ionic liquids in the presence of *p*-Ts at 393 K for 12 h, are listed in Table 1. The molar ratios of *tert*-butyl alcohol with transition metal complex catalyst and *p*-Ts with catalyst were 200 and 100, respectively. The following products were confirmed by GC/MS analysis (Scheme 1) *iso*-butylene (*i*-BE), ethyl *tert*-butyl ether (ETBE), ethyl *tert*-valerate (*t*-EV), ethyl *iso*-valerate (*i*-EV) and the dimer of *iso*-butylene in some cases.

Varied conversions and selectivities were obtained with different transition metal complex + ionic liquid catalyst systems in the presence of *p*-Ts. By-products such as *i*-BE and ETBE may be formed from dehydration of *tert*-butyl alcohol itself, and also from the dehydration reaction between *tert*-butyl alcohol and ethanol in the presence of *p*-Ts. Since GC/MS analysis was not able to confirm whether the desired products in the upper layer were contaminated with *p*-Ts, metal complex catalysts, ionic liquid or not the extent of contamination of the products with *p*-Ts, *etc.*, is not known at this stage. The Au, Co, Cu and Pt triphenylphosphine complexes were less active for hydroesterification of *tert*-butyl alcohol with ethanol (entries 1–4), in which the main reactions were dehydration of *tert*-butyl alcohol itself and the dehydration reaction between *tert*-butyl alcohol and ethanol. When Pt triphenylphosphine complex was used, the dimerization reaction of *iso*-butylene also occurred. Ru triphenylphosphine complexes showed moderate activity for the hydroesterification reaction. In comparison with the catalytic performance of Ru(PPh₃)₄Cl₂ and Ru(PPh₃)₃Cl₂ as catalysts (entries 5, 6),



Scheme 1 Products confirmed by GC/MS analysis.

it can be seen that, although the difference in conversion was not so great, very small amounts of t-EV and i-EV were obtained over Ru(PPh₃)₃Cl₂, indicating that the coordination number of triphenylphosphine to Ru plays an important role in the formation of valerate; however, the reason is still not clear at this stage. Pd was found to be the most effective catalyst for hydroesterification of *tert*-butyl alcohol among these transition metal complex catalysts, which is consistent with the previous work conducted in organic solvents.¹⁷ A *tert*-butyl alcohol conversion of 90.5 and 78.7% total selectivity to t-EV and i-EV were obtained (entry 7). The reasons for the different catalytic performances of these metal complexes on the reaction are not clear at this time and further investigations are needed to explain such differences.

In order to show the easy isolation of the desired products, one example of an isolated yield is given in the case of entry 7. Through only the upper layer was recovered, a total ester yield (t-EV + i-EV) of 60.1 and 96% purity was achieved, which indicates that the desired products are mostly contained in the upper layer.

Under the same reaction conditions, the effect of various ionic liquids on the hydroesterification reaction was examined using Pd(PPh₃)₂Cl₂ as catalyst. The difference in product distribution between different ionic liquids in Table 1 is not remarkable except for MBIm[PF₆]. The ionic liquids employed in this work can be classified as two kinds: miscible or immiscible with water. Ionic liquids that contain [BF₄]⁻ or [NO₃]⁻ are water miscible, and showed roughly similar conversion and product selectivities (entries 8–11). The formation of *iso*-butylene dimer, however, was observed with the water immiscible MBIm[PF₆] (entry 12), which may have some bearing on the difference.

For the purpose of comparison, the same hydroesterification reaction was conducted using Pd(PPh₃)₂Cl₂ in organic solvents (entries 13, 14); it can be seen that the conversion of *tert*-butyl alcohol was relatively lower and no ethyl *tert*-valerate was produced, suggesting that the reaction medium plays an important role in the reaction.

Effect of molar ratios of p-Ts/Pd(PPh₃)₂Cl₂ and *tert*-butyl alcohol/Pd(PPh₃)₂Cl₂ on the hydroesterification of *tert*-butyl alcohol

The effect of the molar ratios of p-Ts/Pd(PPh₃)₂Cl₂ and *tert*-butyl alcohol/Pd(PPh₃)₂Cl₂ on the reaction was investigated and the results are listed in Table 2. No reaction occurred when p-Ts was not used, indicating that p-Ts is indispensable for the carbonylation of *tert*-butyl alcohol (entry 1). As the

molar ratio of p-Ts/Pd increased from 40 to 100, the conversion of *tert*-butyl alcohol and corresponding selectivity to t-EV and i-EV increased while the selectivity to i-BE and ETBE decreased (entries 2–5). When the p-Ts/Pd ratio was further increased (entries 6 and 7), the conversion of *tert*-butyl alcohol and total selectivity to t-EV and i-EV decreased. However, it is worth noting that the variation of the selectivities for t-EV and i-EV exhibit different trends: the former continues to increase, while the later decreases remarkably, indicating that a strong acidic environment is more favorable for t-EV formation. At the same time, selectivities to by-products i-BE and ETBE also increased, and a small amount of i-BE dimer was produced when the molar ratio of p-Ts/Pd was too high.

The effect of the *tert*-butyl alcohol/Pd(PPh₃)₂Cl₂ molar ratio on the reaction was also examined. When Pd(PPh₃)₂Cl₂ was not used, as expected, only i-BE and ETBE were formed, which may result from the dehydration of *tert*-butyl alcohol itself and a dehydration reaction between *tert*-butyl alcohol and ethanol in the presence of p-Ts (entry 8). Upon increasing the molar ratio of *tert*-butyl alcohol/Pd(PPh₃)₂Cl₂, the conversion of *tert*-butyl alcohol decreased correspondingly and the selectivities to desired products (*i.e.*, t-EV and i-EV) and by-products (*i.e.*, i-BE and ETBE) decreased and increased, respectively (entries 9–13).

Effect of pressure, reaction time and temperature on the hydroesterification of *tert*-butyl alcohol

The effects of pressure, reaction time and temperature on the hydroesterification reaction are shown in Table 3. With increasing CO pressure, the conversion of *tert*-butyl alcohol and total selectivity for t-EV and i-EV increased monotonically, entries 1–3 and 5. The maximum selectivity for t-EV was achieved at 6 MPa, the highest pressure used.

The reaction temperature, as expected, has a strong impact on the catalyst performance (entries 4–6). In the region between 373 to 413 K, the conversion of *tert*-butyl alcohol and selectivity to esters increases to their maximum values at 393 K and then decrease when the temperature was further increased. Formation of *iso*-butylene dimer was also observed at the highest temperature, which as higher temperatures are more favorable to the dehydration of *tert*-butyl alcohol to *iso*-butylene and the dimerization of *iso*-butylene.

At 393 K and 6 MPa of CO, the results of entries 5, 7, and 8 show that the conversion of *tert*-butyl alcohol increases with time before leveling off after 18 h. At 18 h, 95% of the *tert*-butyl alcohol has been consumed and both the selectivities to t-EV and i-EV have reached their maximum values.

Table 2 Effect of p-Ts/Pd(PPh₃)₂Cl₂ and *tert*-butyl alcohol/Pd(PPh₃)₂Cl₂ molar ratios on the hydroesterification reaction^a

Entry	p-Ts/Pd(PPh ₃) ₂ Cl ₂	<i>tert</i> -Butyl alcohol/Pd(PPh ₃) ₂ Cl ₂	Conv. (%)	Selectivity (%)				
				i-BE	ETBE	t-EV	i-EV	Dimer
1	0	200	~0	—	—	—	—	—
2	40	200	73.7	13.4	27.9	7.67	50.9	—
3	60	200	86.7	8.7	17.7	12.3	61.3	—
4	80	200	87.0	7.8	16.1	12.5	63.5	—
5	100	200	90.5	7.1	14.1	14.1	64.6	—
6	120	200	89.1	8.6	20.9	14.3	55.5	0.8
7	140	200	81.1	10.8	24.9	15.1	47.4	1.7
8	100	∞ ^b	59.2	23.7	76.3	—	—	—
9	100	100	88.7	8.2	17.2	15.1	59.4	—
10	100	400	75.5	10.2	43.7	7.6	38.2	—
11	100	600	70.3	14.8	53.9	5.9	26.7	—
12	100	800	65.2	29.0	61.9	2.1	9.4	—
13	100	1000	63.3	26.4	66.3	1.2	5.9	—

^a Reaction conditions: MEIm[BF₄], 6.0 MPa CO, 393 K, 12 h, *tert*-butyl alcohol: 0.017 mol. ^b In the absence of Pd(PPh₃)₂Cl₂.

Table 3 Effect of pressure, reaction time and temperature on the hydroesterification^a

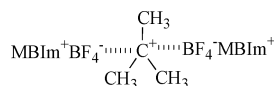
Entry	P/MPa	t/h	T/K	Conv. (%)	Selectivity (%)				
					i-BE	ETBE	t-EV	i-EV	Dimer
1	3	12	393	70.7	17.6	47.2	6.3	30.2	—
2	4	12	393	78.1	13.3	33.3	10.5	46.5	—
3	5	12	393	85.1	12.6	30.8	9.7	46.7	—
4	6	12	373	78.8	10.1	26.7	7.5	55.6	—
5	6	12	393	90.5	7.1	14.1	14.1	64.8	—
6	6	12	413	66.7	10.3	33.7	4.3	25.2	25.4
7	6	6	393	88.4	4.01	15.5	13.8	66.7	—
8	6	18	393	95.1	1.1	2.1	24.4	72.4	—

^a Reaction conditions: MEIm[BF₄], molar ratio of p-Ts/Pd(PPh₃)₂Cl₂: 100, molar ratio of *tert*-butyl alcohol/Pd(PPh₃)₂Cl₂: 200, *tert*-butyl alcohol: 0.017 mol.

Possible reaction route for the formation of ethyl *tert*-valerate in ionic liquids

A reaction route for hydroesterification *tert*-butyl alcohol in organic solvents was reported previously,¹⁷ involving the conversion of *tert*-butyl alcohol to *iso*-butylene in the presence of an acid substance, followed by carbonylation of *iso*-butylene catalyzed over transition metal complexes; only *iso*-valerate was produced. Carbonylation of *tert*-butyl alcohol in strong acid medium proceeds by a different route.²² *tert*-Butyl cation is firstly formed from *iso*-butylene, which is derived from dehydration of *tert*-butyl alcohol in the presence of H⁺, then *tert*-butyl cation reacts with CO to form an intermediate acylation species, which is hydrolyzed to produce *tert*-acid or ester if water or another alcohol is present.

In this work, both ethyl *tert*-valerate and ethyl *iso*-valerate were produced simultaneously. The facts that no reaction occurred without p-Ts and that a strong acidic environment was more favorable for ethyl *tert*-valerate formation indicates that the formation of ethyl *tert*-valerate may follow the same reaction route as that outlined above in strong acid medium. However, different product distributions were observed when organic solvents or ionic liquids were used as reaction media, which could be reasonably attributed to their different nature. Ionic liquids are ionic solvents that consist entirely of ions and possess a strong static field. This strong static field can probably stabilize the *tert*-butyl cation (Scheme 2), leading to the formation of ethyl *tert*-valerate in ionic liquids. In organic solvents, this stabilization is absent and the reaction follows another route and only ethyl *iso*-valerate formation is observed.



Scheme 2 A possible stabilization of *tert*-butyl cation in ionic liquids.

Conclusion

Hydroesterification of *tert*-butyl alcohol with ethanol catalyzed by transition metal triphenylphosphine complexes was

performed in room temperature ionic liquids as reaction medium in the presence of p-Ts. Higher conversion was achieved and ethyl *tert*-valerate could be directly formed in the ionic liquid medium in comparison to organic solvents as reaction medium. The products could be separated from the ionic liquids easily due to their immiscibility with the ionic liquids. The ionic liquids and transition metal triphenylphosphine complex catalyst system can be further optimized. These results suggest that ionic liquids could be a promising reaction medium for clean and efficient synthesis of pivalic acid.

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