Synthesis of esters under microwave irradiation using heteropoly acids as catalysts

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A practical and simple technique for synthesis of esters was developed by using heteropoly acid as catalyst under microwave irradiation in the absence of organic solvents. Alcohols were easily and selectively converted to their acetates and benzoates with excellent yields (≥98%), and in very short time (~5 min), as environmentally benign.

KEY WORDS: catalysis; esters; heteropoly acid; microwave; synthesis.

1. Introduction

Esters are important industrial products, usually synthesized by esterification of carboxylic acids, transesterification of methyl or ethyl esters, and alkylation of carboxylate anions [1]. The first type of reaction is generally catalyzed by mineral acids, and the conversion of alcohol to esters is an important industrial functional group transformation. The second major class of alcohol protecting groups are the esters. Although there are several esters, acetates and benzoates can be and likely have been used in protecting alcohols, due to their propensity for acyl substitution and hydrolysis [2].

The eco-friendly green approach has lately been expanded with the development of increasingly clean chemical procedures, and inorganic catalysts provide a number of advantages of environmental interest, including easy isolation and recovery from the reaction medium [3].

Among the acid catalysts, heteropoly acids have probably received the greatest attention, because of their high acidity strength and selectivity properties, and their catalytic activities are much higher than those of H_2SO_4, HNO_3 and $HClO_4$ [4,5]. In general, these acids are green and efficient bifunctional catalysts when combined with other components [6,7].

In an earlier study [8], tungstosilicic acid was used as a catalyst and ethyl acetate was obtained with a yield to 99.5% (vapor-phase esterification at 150 °C during 4–7 h), and many esterification reactions were studied using heteropoly acids as catalysts [9–12].

The application of microwave heating techniques in synthesis has attracted considerable interest in recent years, and many reviews were published in the past five years [13–16]. The first use of microwaves for the synthesis of esters started with the esterification of benzoic acid with methanol, propanol and butanol [17], and several studies have been performed to investigate the influence of microwave irradiation on the rate of esterification reactions [18–24]. To our knowledge no articles have been published on heteropoly acid and microwaves used together on the esterification reactions.

In our laboratory, studies on the preparation and application of heteropoly acids [25,26] and microwave-assisted [27–29] reactions have been continuing. We have developed an easy-going solvent-free procedure for preparation of acetates and benzoates, using heteropoly acid and microwave energy together, as presented in this work.

2. Experimental

The catalysts $H_4PVMo_{11}O_{40}$, $H_{0.5}Cs_{2.5}PMo_{12}O_{40}$ and $(NH_4)_6HPV_4W_9O_{40}$ were prepared in our laboratory [25,26], and $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ were purchased from Riedel and Merck. All other chemicals were supplied by Fluka and Merck, and esterification reactions were performed in Teflon vessels. Microwave irradiation was carried out with a commercial microwave oven (CEM MDS 2000). Gas chromatograpy analyses were performed with a Unicam 610 instrument fitted with a capillary (30 m × 0.25 mm i.d. = 0.5 μm film) column packed with (78% cyanopropyl) methyl polysiloxane. IR spectra and refractive indexes (n_D) were measured using a Midac 1700 FTIR spectrophotometer and an Atago refractometer respectively.

The esters were prepared by the reaction of alcohols (butanol, heptanol, octanol and benzyl alcohol) with acetic acid and benzoic acid, using heteropoly acids or

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Table 1
Esterification by $H_3PW_{12}O_{40}$ (0.05 mmol) under microwave irradiation (5 min)

$$RCOOH + R'OH \overset{\text{catalyst}}{\rightleftharpoons} RCOOR' + H_2O$$

R	R′	Alcohol/acid (mmol/mmol)	Power (%)	Yield [a] (%)	Yield [b] (%)	Yield [c] (%)	t_R [d]	n_D^{20}
CH_3	C_4H_9	25/50	30	99.7	18.0	91.0	60	1.3951
CH_3	C_7H_{15}	10/15	30	98.6			88	1.4152
CH_3	$C_6H_5CH_2$	15/30	30	98.0			93	1.5028
C_6H_5	C_7H_{15}	2/5	80	99.0			48	1.4400
C_6H_5	C_8H_{17}	2/5	80	98.0			53	1.4725

[a] Reactions in microwave using $H_3PW_{12}O_{40}$ catalyst.
[b] Reactions in microwave using H_2SO_4 catalyst, yield obtained by distillation.
[c] Reactions with conventional heating using $H_3PW_{12}O_{40}$ catalyst.
[d] GC retention time.

H_2SO_4 as catalysts under microwave irradiation or conventional heating.

$$R{-}COOH + R'{-}OH \overset{\text{catalyst}}{\rightleftharpoons} R{-}COOR' + H_2O$$

A variety of reaction conditions such as microwave power, microwave irradiation time, alcohol/carboxylic acid ratio, catalyst types and concentrations were tested. Thus, for solvent-free conversion of alcohols to esters over 70 experiments were performed under different reaction conditions.

2.1. Typical experimental procedure

$H_3PW_{12}O_{40}$ was mixed thoroughly with a mixture of alcohol and carboxylic acid in the proportions indicated in table 1, and irradiated in a microwave system or refluxed. The cooled mixture was shaken with distilled water, and heteropoly acid was completely extracted into the aqueous phase. The organic layer was dried over anhydrous Na_2SO_4. After separation of the salt, the organic phase was distilled under vacuum and investigated for analysis.

3. Results and discussion

Our preliminary studies on the preparation of heptyl acetate showed that the efficiency of catalysts is related to the strength of the acidity, and the order of catalyst efficiency is

$$H_3PW_{12}O_{40} > H_3PMo_{12}O_{40} > H_4PVMo_{11}O_{40} \gg H_{0.5}Cs_{2.5}PMo_{12}O_{40} > (NH_4)_6HPV_4W_9O_{40}$$

(yield of the ester: $92 > 89 > 65 \gg 9 > 7$), in agreement with the earlier statements on the related reactions [4,5]. Thus, $H_3PW_{12}O_{40}$ is the best catalyst to promote the equilibrium shifting and was used in the experiments. Catalysts may be divided into two classes, homogeneous ($H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $H_4PVMo_{11}O_{40}$) and heterogeneous ($H_{0.5}Cs_{2.5}PMo_{12}O_{40}$, $(NH_4)_6HPV_4W_9O_{40}$). The reactivity order in the former is

$$H_3PW_{12}O_{40} > H_3PMo_{12}O_{40} > H_4PVMo_{11}O_{40},$$

while the order in the latter is

$$H_{0.5}Cs_{2.5}PMo_{12}O_{40} > (NH_4)_6HPV_4W_9O_{40}).$$

On the other hand, in order to investigate the effect of the ratio of the alcohol/carboxylic acid, the ratios were changed between 0.1 and 10, and to prevent etherification and related other reactions [29], the values <1 were selected (table 1). For comparison, similar reactions were carried out in conventional ways in the presence of heteropoly acids and also in a microwave in the presence of H_2SO_4.

To determine the effect of microwave power on the esterification rate, different power stages (%) 10 (63 W), 20 (126 W), 30 (189 W), 60 (378 W) and 80 (504 W) were applied at various times for the preparation of esters. As can be seen from figure 1 the yield (%) of heptyl acetate increases rapidly with the power level increasing up to ~150 W, and there is no significant difference in the rate of esterification over this power value.

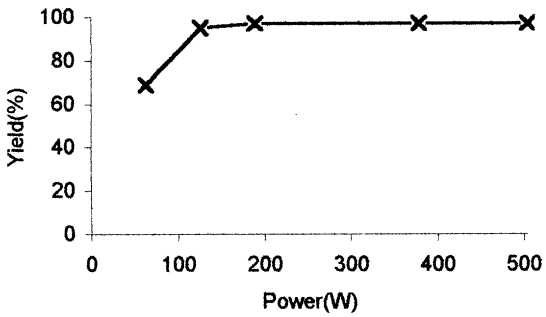

Figure 1. The effect of microwave power on esterification of acetic acid and heptanol. Catalyst: 0.05 mmol $H_3PW_{12}O_{40}$. Irradiation time: 5 min.

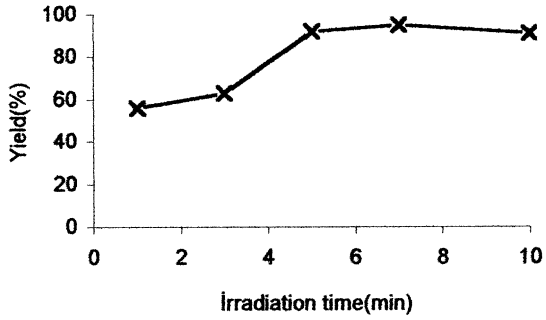

Figure 2. Effect of the irradiation time on esterification of acetic acid and heptanol. Catalyst: 0.05 mmol $H_3PW_{12}O_{40}$. Microwave power: 30%.

The next set of experiments was performed by observing the effect of microwave irradiation time on the production of heptyl acetate (figure 2). The results show that an excellent yield was obtained with ~5 min of the irradiation-reaction time at a fixed power of 30%. Reaction times in the synthesis of esters when using heteropoly acids as catalysts may take place over several hours using conventional handling [4,5,10]. It was observed that the required reaction time to produce esters was decreased by increasing the microwave energy power. To check these possibilities, further work is in progress.

The effect of catalyst concentration on the yield was also studied (figure 3), showing a saturation-like curve. At 0.05 mmol, maximum catalyst yield was achieved. FTIR spectra values (cm^{-1}) for heptyl acetate are 2955, 2938, 2873, 1729, 1456, 1356, 1049 and for heptyl benzoate are 3056, 2947, 2863, 1728, 1461, 1362, 1288, 1103, and boiling point values of the same esters are 50 °C (0.1 mmHg) and 90 °C (0.1 mmHg) respectively.

The obtained information on the other esters is similar within experimental error; thus, to avoid repetition, these results are not presented, and total results are summarized in table 1. The results show that the investigated alcohols were easily and selectively converted to their acetates and benzoates with excellent yields (≥98%), and very short times (~5 min), in the absence of environmentally undesirable solvents, catalysts and side products.

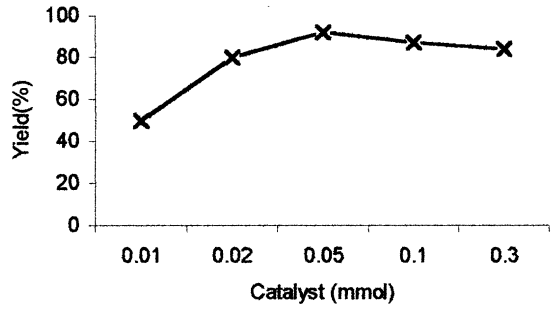

Figure 3. The effect of $H_3PW_{12}O_{40}$ concentration on the esterification of acetic acid and heptanol. Microwave power: 30%. Irradiation time: 5 min.

4. Conclusions

We have demonstrated that the synthesis of esters from alcohols and carboxylic acids can be accomplished by novel and rapid methods using heteropoly acids as catalysts under microwave irradiation, in the absence of solvent.

Finally, the proposed method is a combination of heteropoly acid and microwave energy for the synthesis of ester, allowing shortening of the reaction time from hours to minutes as environmentally benign.

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