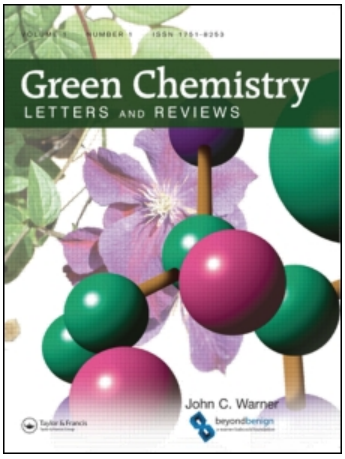

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RESEARCH LETTER

Green synthesis of isoamyl acetate in glycerol triacetate

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Glycerol triacetate was successfully used as a green solvent and as the acyl donor in the production of isoamyl acetate by the transesterification of isoamyl alcohol over an acidic ion-exchange resin. Using glycerol triacetate as the solvent also enabled simple product recovery, easy catalyst separation and recycling, and microwave-promoted heating.

Keywords: glycerol triacetate; solid acid; catalyst; isoamyl acetate

Introduction

As environmental concerns become more important, the search for green methods of producing fine chemicals, the synthesis of which is usually associated with air, water, and land contamination and the disposal of large amounts of waste, is a significant challenge (*1*). The environmental impact of any synthetic procedure depends on the toxicity and volatility of the reagents and the solvent, the amount of energy consumed during the reaction, whether by-products are generated that should be separated at the end of the reaction, and ease of catalyst separation and product purification (*2*).

Organic esters are important intermediates in the synthesis of fine chemicals, plasticisers, pharmaceuticals, perfumes, cosmetics, and food additives. Although many esters are obtainable from plants, the extraction process, which involves the use of organic solvents, is costly, inefficient, and associated with the production of large amounts of waste. Alternatively, an alcohol can be esterified via several catalytic routes, each with its particular advantages and disadvantages, using different homogeneous and heterogeneous chemo and bio-catalysts (*3*).

Here we report on the green transesterification of isoamyl alcohol using the acidic ion-exchange resin, Amberlyst 36 as a catalyst and triacetin as both an acyl donor and as a solvent (Figure 1). Using triacetin enabled easy isolation of the product by simple extraction with petroleum ether or distillation, separation and recycling of the catalyst, and microwave-promoted heating.

Results and discussion

Isoamyl acetate is one of the most widely used short-chain esters in the food industries because of its characteristic banana flavor (*4*). It can be produced from isoamyl alcohol by several catalytic reactions distinguishable by the type of acyl donor involved (*4–7*). Direct esterification of isoamyl alcohol with acetic acid is the most straightforward synthetic procedure, as it produces only water as a by-product. However, being an equilibrium reaction, direct esterification usually requires that the corrosive acid be present in excess and that the water by-product be removed during the reaction to reach a high ester yield. Alternatively, acylation of the alcohol, which is not an equilibrium reaction, is also possible, but the use of either toxic acyl chloride or acetic anhydride as the acyl donor generates hydrochloric acid or acetic acid, respectively, as by-products, and thus it requires special equipment and treatment. In addition, acylation usually involves a hazardous organic solvent. Finally, transesterification of isoamyl alcohol by adding an ester, such as ethyl acetate is also feasible and yields isoamyl acetate and ethanol.

The catalysts for all types of alcohol esterification can be either homogeneous or heterogeneous acids and bases, or free or immobilized lipases (*4–7*). Although a soluble, strong mineral acid such as sulfuric acid is traditionally used as the esterification catalyst, a solid acid such as a zeolite, sulfated zirconia, or acidic ion-exchange resins, is preferable as it can be easily separated by filtration and re-used, a neutralization step is not required at the end of the reaction, and large amounts of waste are not released (*5*).

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Figure 1. Transesterification of isoamyl alcohol in triacetin.

In light of the considerations mentioned above, glycerol triacetate (triacetin) was selected as the solvent and the acyl donor for the catalytic transesterification of isoamyl alcohol over Amberlyst 36 (Figure 1). Triacetin is a clear, colorless, non-toxic ester with a variety of applications in foods and flavors, dyes and inks, and the cosmetics industries. Its physical properties also make it an attractive solvent. Its high boiling point and low vapor pressure enable product distillation, while extraction of the product is also possible with triacetin immiscible solvents such as ethers.

The transesterification of isoamyl alcohol in triacetin under mild conditions without pretreating the catalyst resulted in 13% conversion after 1 h (Table 1, entry 1). Because pretreatment of the solid catalyst is known to possibly affect its catalytic performance, the effect of catalyst preheating temperature and time on isoamyl alcohol conversion was tested. Preheating the solid catalyst at 80°C for 1 h yielded the highest isoamyl alcohol conversion of 20% (entry 2). Therefore, the catalyst was preheated at 80°C for 1 h for all subsequent experiments of the study. Increasing either reaction temperature or catalyst loading linearly increased isoamyl alcohol conversions (entries 3–4 and 5–6, respectively), which also increased as the reaction progressed, achieving full conversion after 14 h at 60°C (entries 7–9). Recycling of the heterogeneous catalyst was also tested by catalyst filtration and re-use by adding it to fresh isoamyl alcohol in triacetin (entries 10–11). With each reaction cycle, the catalyst lost some of its activity.

Because triacetin was added in excess, the efficacy of recycling both the triacetin and the catalyst was also examined by extracting the isoamyl acetate from the reaction mixture at the end of the reaction with petroleum ether and adding fresh isoamyl alcohol. This method also resulted in partial catalyst deactivation, yielding even lower conversions than those detected when only the catalyst was recycled (Table 1, entries 12–13). Such low conversion can be explained by the partial conversion of triacetin to glycerol, glycerol mono-acetate, or glycerol di-acetate, as detected by H-NMR analysis of the reaction mixture, all of which may facilitate the reverse reaction.

Finally, microwave-promoted heating was recently reported to enhance organic reactions, including the hydrolysis of esters, relative to conventional heating (*8–10*). Thus, using an unmodified, home microwave at full intensity, the transesterification of isoamyl alcohol in triacetin under microwave irradiation was also tested in an open reaction vessel, with Amberlyst 36 as the catalyst, for 10–60 s. Heating the reaction mixture for up to 40 s without adding the catalyst increased the temperature from 26 to 123°C but did not yield any isoamyl acetate. With the catalyst, however, the reaction proceeded rapidly, and the rate was 100-fold higher than for the reaction under conventional heating. For example, the microwave-promoted

Table 1. Amberlyst 36-catalyzed transesterification of isoamyl alcohol in triacetin.[a]

Entry	t (h)	T (°C)	Catalyst amount (g)	Conversion (%)
1[b]	1	60	0.1	13
2	1	60	0.1	20
3	1	70	0.1	32
4	1	80	0.1	41
5	1	60	0.2	40
6	1	60	0.3	59
7	4	60	0.1	55
8	7	60	0.1	78
9	14	60	0.1	97
10 (second cycle)[c]	14	60	0.1	85
11 (third cycle)[c]	14	60	0.1	60
12 (second cycle)[d]	14	60	0.1	70
13 (third cycle)[d]	14	60	0.1	38

[a]Reaction conditions: 5 g triacetin, 0.1 g isoamyl alcohol. The catalyst was preheated at 80°C for 1 h.
[b]Without pre-heating of the catalyst.
[c]Recycling of the catalyst after filtration from the reaction mixture and addition to a fresh mixture of isoamyl alcohol and triacetin.
[d]Recycling of the catalyst and the triacetin after extraction of the product without previous separation of the catalyst and addition of fresh isoamyl alcohol.

reaction yielded 12% conversion after 20 s and reached a final temperature of 67°C, while the reaction that was performed in an oil bath at 60°C reached 20% conversion after 1 h. To the best of our knowledge, the microwave-assisted organic synthesis of ester hydrolysis has never been reported at such an accelerated rate. It seems that although triacetin has a relatively low dielectric constant, the production of glycerol di- and mono-acetate and glycerol as by-products of the transesterification of triacetin increases the polarity of the reaction medium, thereby augmenting the ability of the reaction mixture to adsorb microwave irradiation (*10*). Furthermore, the markedly low vapor pressure and high boiling temperature of triacetin make it an attractive solvent for microwave-promoted organic synthesis under atmospheric pressure.

Changes in the final temperature of the reaction medium and in the conversion of isoamyl alcohol with the reaction time are illustrated in Figure 2. Both the final temperature and the conversion of isoamyl alcohol increased linearly with the progress of the reaction up to 40 s. Increasing the time over 40 s while heating the reaction medium at full intensity raised the temperature of the medium above 130°C, but this high temperature severely damaged the catalyst. Increasing the isoamyl concentration from 0.23 to 2.3M, while maintaining catalyst loading, increased the transesterification six-fold from 0.053 to 0.32M isoamyl acetate. Furthermore, performing the reaction for 20 s (final reaction temperature of 67°C) for two sequential cycles, between which the reaction mixture was cooled to room temperature in ice, yielded a 12% conversion after the first cycle and a 19% conversion after the second cycle.

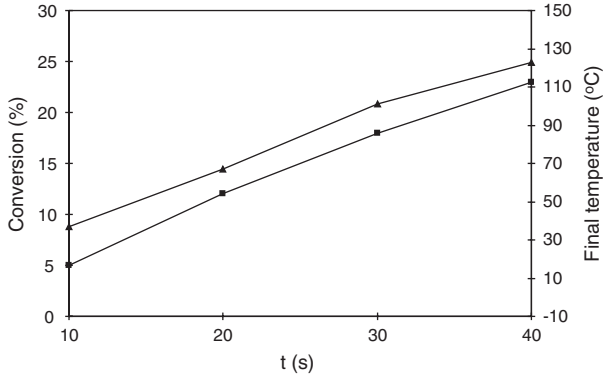

Figure 2. Transesterification of isoamyl alcohol in triacetin by microwave-assisted heating: conversion (■) and final temperature (▲). Reaction conditions: 5 g triacetin, 0.1 g isoamyl alcohol, and 0.1 g Amberlyst 36.

Experimental

In a typical procedure, 0.1 g of isoamyl alcohol and 0.1 g of Amberlyst 36 were added to a vial with 5 g of triacetin (all purchased from Aldrich). The mixture was placed in a preheated oil bath and heated to the required temperature (40–80°C) after which it was magnetically stirred for 1–14 h. At the end of the reaction, the reaction mixture was cooled and extracted with 3×10 mL petroleum ether. The organic phase was concentrated under reduced pressure, and the resulting crude product was analyzed by GC analysis using an HP-5 column ($30\ m \times 0.25$ mm, 0.25 μm thick).

Microwave-assisted reactions were conducted at atmospheric pressure in a domestic microwave (Crystal WP900, 900W) in a vial, which was covered with a watch glass. The substrate was dissolved in 5 g triacetin followed by addition of the catalyst. After the vial was covered with the watch glass, the reaction mixture was heated in the microwave oven at full intensity from 26 to 60°C for duration of 10 s and from 26 to 118°C for 40 s. At the end of the reaction the vial was cooled to room temperature in ice, and the reaction mixture was extracted with petroleum ether for GC analysis.

Conclusions

A green protocol for the synthesis of isoamyl acetate from isoamyl alcohol was proposed using glycerol triacetate as both the solvent and as the acyl donor and Amberlyst 36 as the catalyst. Using triacetin in the reaction facilitated efficient separation of the product from the catalyst and recycling of the catalyst, and it allowed the conventional heating method to be replaced with the more efficient microwave-promoted heating. The conversion of isoamyl alcohol was increased by increasing the reaction time and the temperature while maintaining the loading of the catalyst. Heating the reaction in an unmodified home microwave instead of using conventional heating resulted in a 100-fold higher reaction rate.

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