

Kinetics of β -citronellyl acetate synthesis by acid-catalyzed transesterification

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Highlights

- β -Citronellyl acetate synthesis responds to principles of green chemistry.
- High conversion and selectivity were obtained using *p*-toluene sulfonic acid and ethyl acetate.
- The kinetics was dependent on amount of acid catalyst and chain length of alkyl.

1. Introduction

Recently, there has been an effort to choose a raw material based on a renewable resource instead of using crude oil, natural gas, and coal. One of the many options is the use of essential oils from plants that are rich on monoterpenes and its derivatives – monoterpenoids [1]. These fragrant compounds with a characteristic scent often possess positive biological activity on the organisms (e.g., analgetic, anti-inflammatory).

β -Citronellyl acetate is used for its flower tones or citrus nuances, and can be synthesized from citronellol, which is contained in rose and geranium, lemongrass, and lemon eucalyptus [2]. Ways and means of synthesis are more – reaction with acetic anhydride, acetic acid, or alkyl acetate, and under various conditions. The transesterification of alkyl acetate under conditions of acid catalysis was chosen (Figure 1) in this work. This type of reaction with β -citronellol was not often studied and conforms to the principles of green chemistry.

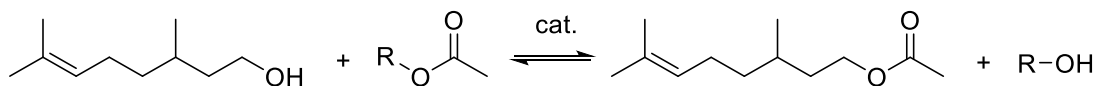


Figure 1. Scheme of transesterification of β -citronellol

This work aimed to the study of transesterification kinetics using different alkyl acetates. The part of the work deals with the finding of optimal reaction conditions (type and amount of acid catalyst, reactants molar ratio, temperature) with suitable alkyl acetate and reaction arrangement (with and without reactive distillation).

2. Methods

Experimental. The reaction was performed in a 25 mL two-necked round bottom flask with a condenser heated in an oil bath on a magnetic stirrer and vigorous stirring. Collected samples of the reaction mixture were neutralized and centrifuged. The neutral organic layer was diluted, and the composition was analyzed by gas chromatography with a flame ionization detector (GC-FID) and non-polar column. Compounds were identified using gas chromatography with mass spectrometry detection.

Calculation of kinetics. The conversion and selectivity were calculated from the composition of the reaction mixture, which was found out by GC-FID. The molar concentration of substances was calculated from initial composition and the analysis of conversion and selectivity. In the kinetic model, side, and sequence reactions for forming the by-products were considered. For calculation, the program MATLAB was used. Reaction rate constants and activation energies were evaluated.

3. Results and discussion

The kinetics (Figure 2) of transesterification was dependent on catalyst amount (*p*-toluene sulfonic acid, PTSA); with higher amount of catalyst the reaction rate increased. Similar results offered 10 and 12 mol. % of PTSA. The comparison of the different alkyl acetates used for transesterification (ethyl

acetate and *n*-butyl acetate) is also presented in Figure 2. It was interesting that the kinetics of transesterification with *n*-butyl acetate and 10 mol. % PTSA was similar as kinetics with ethyl acetate and 5 mol. % PTSA. However, it corresponded to the twice higher catalyst amount and twice longer alkyl chain. It is clear that *n*-butyl acetate was less reactive than shorter alkyl acetate – ethyl acetate. We can see the relatively high conversion (between 70 % and 80 % at 6 h) at mild temperature 50 °C. For all studied reaction, the high selectivity for β -citronellyl acetate was observed, around 95 %. α -Citronellol (isomer of β -citronellol), α -citronellyl acetate, hydroxycitronellyl acetate, dicitronellyl ether were detected as undesired by-products.

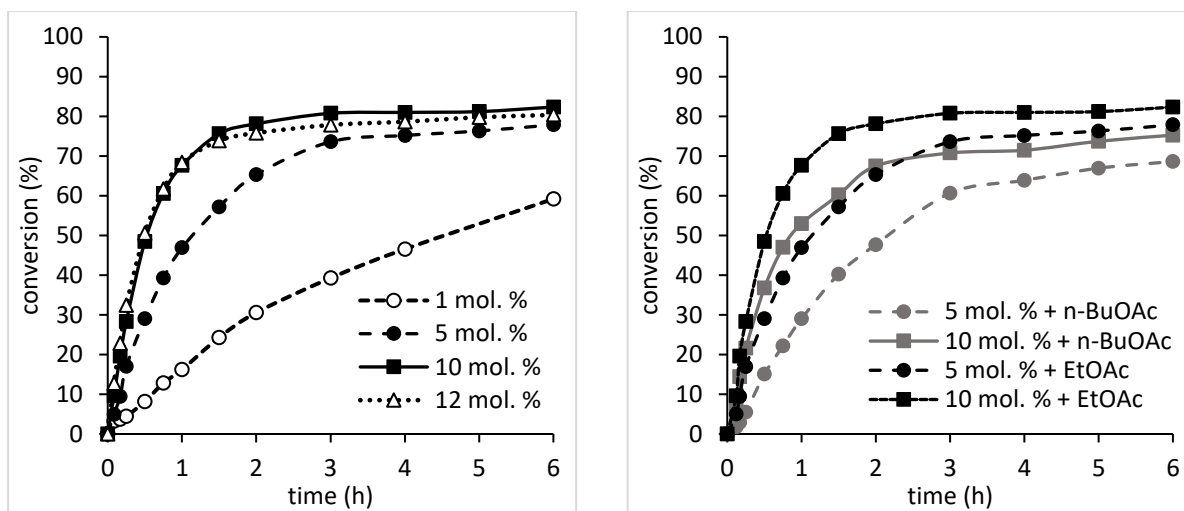


Figure 2. Dependence of conversion of citronellol on time ($n(\text{citronellol}) : n(\text{alkyl acetate}) = 1:3$, 50 °C):
left – influence of the amount of *p*-toluene sulfonic acid with ethyl acetate,
right – comparison of reactivity of different alkyl acetate with the same amount of *p*-toluene sulfonic acid

4. Conclusions

The transesterification of alkyl acetates by β -citronellol under mild acid-catalyzed conditions proceeded with high conversion and a high selectivity to β -citronellyl acetate. 80 % conversion with 95 % selectivity was achieved at 3 hours using following conditions with ethyl acetate and 10 mol. % of PTSA as catalyst. The kinetic evaluation showed reaction rate constants, and activation energies and we can conclude that this reaction arrangement may serve as a base for the industrial production of β -citronellyl acetate.

References

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Keywords

Kinetics; biorenewable resources; citronellyl acetate; transesterification.