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Laboratory Experiment

Transesterification of Isoamyl Acetate—An Experiment in Green Organic Chemistry

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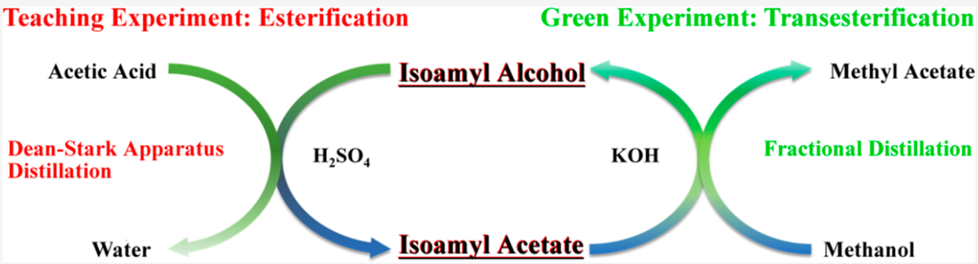

ABSTRACT: Applying the idea of green chemistry, we extended an esterification teaching experiment with isoamyl alcohol and acetic acid and reused isoamyl acetate in the transesterification reaction with KOH as the catalyst. As a result, isoamyl alcohol was produced and could be reused for the teaching experiment. The simplified experimental method achieved high purity for the product. This esterification reaction does not produce more waste liquid, and because the isoamyl alcohol can be reused, the cost of reagent procurement and waste liquid disposal is reduced. This green experiment offers not only environmental benefits but also an important learning experience for students. It improves their skills and cultivates a consciousness of innovation and environmental protection.

KEYWORDS: *Organic Chemistry, Green Chemistry, Transesterification, Isoamyl Acetate, Methanol, Isoamyl Alcohol, Methyl Acetate*

■ INTRODUCTION

With increasing global environmental pollution and excessive use of energy resources, "green chemistry" has become a hot topic not only in academic research but also as a development direction for industrial production.[1,2] Green chemistry, also known as environmentally friendly chemistry, refers to the effective use of (preferably renewable) raw materials, the elimination of waste, and the avoidance of toxic or dangerous reagents in the manufacture and application of chemical products.[3−6] Conserving resources and protecting the environment are fundamental goals of "green chemistry" and foster a harmonious and sustainable lifestyle. Applying green chemistry knowledge in teaching not only improves teaching quality but also cultivates students' sense of responsibility for environmental protection.[7−10]

Organic Chemistry Experiment is a basic course at Dalian University of Technology for sophomores majoring in chemistry and chemical engineering. The course is also an important practical session in terms of enhancing students' awareness of green chemistry. The experiments require a lot of reagents and inevitably produce waste. Products which are refined by students are often treated as waste. With the increasing awareness of energy conservation and environmental protection, many educators are applying the concept of green chemistry when teaching experimental classes by revising the design of experiments to reduce environmental pollution.[11−17] In the teaching experiment for the preparation of isoamyl acetate offered by the Chemical Experiment Center of Dalian University of Technology, at least 2 L of isoamyl acetate is disposed as waste every year.[18,19] Similarly, the methanol recovered in the liquid chromatography experiment is treated as waste liquid; the cost for disposal of these reagents is high. This paper reports a green chemistry experiment using recycled isoamyl acetate and methanol to generate isoamyl alcohol through a transesterification reaction catalyzed by KOH.[20−22] The isoamyl alcohol can be reused as the reaction raw material in the teaching experiment for the preparation of isoamyl acetate. In this way, we established a cycle with the original teaching experiment to reduce the discharge of waste and recycle the resources.[23−25] We hope that the experiment will inspire students' interest in applying the knowledge to solve practical problems, and enhance their consciousness of environmental protection and innovation.

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$$CH_3COOCH_2CH_2CH(CH_3)_2 + CH_3OH \underset{\Delta}{\overset{KOH}{\rightleftharpoons}} CH_3COOCH_3 + (CH_3)_2CHCH_2CH_2OH \quad (1)$$

The transesterification reaction of isoamyl acetate with methanol is shown in formula 1. Isoamyl acetate and methanol are transformed into isoamyl alcohol and methyl acetate in the presence of KOH. In our experiment, adding excess methanol and removing methyl acetate through fractional distillation ensured a high yield of isoamyl alcohol because the transesterification reaction is reversible. In addition to improving the conversion rate of isoamyl acetate, the formation of an azeotrope of methanol and methyl acetate also required excess methanol. The reaction began at a low temperature, and only the azeotrope of methanol and methyl acetate were separated from the reaction system. When the temperature rose to the boiling point of isoamyl alcohol, high purity of the obtained isoamyl alcohol was achieved.

■ EXPERIMENTAL DETAILS

In a typical green experiment, 2.8 g of KOH and 16 mL (0.40 mol) of methanol were added to a 100 mL round-bottom flask. Then 13.1 g (0.10 mol) of dried isoamyl acetate was added to the vial. A fractional distillation device was set up, as shown in Figure S1c. The reaction was first refluxed for a period of time and the temperature was gradually increased to collect the mixture of methanol and methyl acetate below 66 °C. Then the reaction system was further heated to collect the 128−132 °C fraction, and 6.2 g of isoamyl alcohol was obtained.

Only a small amount of impurities was separated from the system with methyl acetate and methanol, showing that the purity of isoamyl alcohol was very high and no further treatment was needed. Isoamyl acetate and isoamyl alcohol can be identified by gas chromatography, and the results for this are shown in Figure S2b. Theoretically speaking, all isoamyl acetate can be transformed into isoamyl alcohol. However, the yield of isoamyl alcohol usually decreases due to fractional distillation.

Although used methanol and methyl acetate can be recovered separately, they are not useful and should be treated as organic waste. Students who are interested in recycling can collect them separately.

■ HAZARDS

The solvents used in this experiment included isoamyl acetate, methanol, and isoamyl alcohol. Methyl acetates are flammable solvents of moderate toxicity. KOH is corrosive and a strong irritant to skin. Therefore, when conducting the experiment, students must wear goggles and disposable gloves and complete the experiment in the fume hood to ensure their own safety.

■ RESULTS AND DISCUSSION

It took about 30 min to collect 6.2 g (0.07 mol) of isoamyl alcohol in this green transesterification experiment. The gas chromatography detection (see the Supporting Information) showed that the product had high purity and could be recycled for the synthesis of isoamyl acetate.

We combined this experiment with the teaching experiment for the preparation of isoamyl acetate. The product from that teaching experiment was used as the raw material in the green experiment for transesterification of isoamyl acetate to form a complete closed-loop process system (shown in Figure 1).

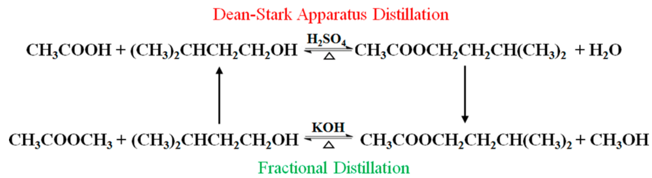

Figure 1. Flowchart of cyclic experiment.

When students carried out these two experiments, about 80% of isoamyl alcohol was converted into isoamyl acetate and almost 70% of the isoamyl acetate was transformed into isoamyl alcohol. As a result, the purchase cost of isoamyl alcohol could be halved, since about 50% of it is reused. These measures can effectively improve the utilization efficiency of chemical reagents and reduce waste. If all the isoamyl acetate in the laboratory was reused (2 L per year), more than 500 RMB yuan per year could be saved.

$$CH_3COOCH_2CH_2CH(CH_3)_2 + R\text{-}OH \underset{\Delta}{\overset{KOH}{\rightleftharpoons}} CH_3COOR + (CH_3)_2CHCH_2CH_2OH \quad (2)$$

Formula 2 shows that isoamyl acetate can interact with water, methanol, ethanol, and other substances. As shown in Table 1, the boiling point of ethanol is only 78 °C, which is close to that of ethyl acetate and their azeotrope point, so the efficiency of transesterification is relatively low. Isoamyl acetate can also react with water to produce sodium acetate and isoamyl alcohol under alkaline conditions. However, isoamyl alcohol and water form an azeotrope at 95 °C, and the separated crude product contains water, which must be refined by liquid separation, drying, filtration, distillation, and other procedures. In this process, significant loss of product is inevitable. In comparison, methanol is a much more efficient reactant. Although the boiling point of methanol is only 64.7 °C, the boiling point of methyl acetate and their azeotrope point are still much lower, which makes methyl acetate more separable from the reaction system. Accordingly, the conversion rate and purity of isoamyl alcohol are both higher. It can be directly seen from Table 1 that the efficiency of transesterification with methanol is better in comparison with the temperature and composition of pure substance and azeotrope. Moreover, methanol is the waste liquid recovered by the experiment for using liquid chromatography, so this component of chemical reagents can be utilized effectively.

Table 1. Boiling Point and Azeotrope Point of Reactants and Products[26]

R	CH_3CH_2	CH_3	H
reactant/boiling point, °C	ethanol/ 78.3	methanol/ 64.7	H_2O/ 100.0
products/boiling point, °C	ethyl acetate/ 73.9	methyl acetate/ 57.8	acetic acid/ 117.9
azeotrope boiling point of reactants and products, °C	71.8	53.6	−
composition, wt %	31.0% ethanol	19.5% methanol	

Because the teaching hours of the experiment course are limited, we have encouraged students to practice the transesterification reaction voluntarily after completing the teaching experiment for transesterification preparation of isoamyl acetate. Because of the simple operation (fractional

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distillation only) and the short reaction time of less than 30 min, this experiment can be used as a supplement to the instructional experiment for students who are capable of and interested in green chemistry. In fact, our undergraduate students won the first prize in the First Liaoning Province Chemical Experiment Competition with this project. Since 2019, about 80 sophomores chose to conduct this green experiment independently. After the experiment, students use gas chromatography or a refractometer to detect the products. We assessed students' experience with this green experiment, and the participating students responded that they were interested in the design concept of green chemistry and happy to contribute to environmental protection by reducing chemical waste. All the participating students have successfully completed this experiment and achieved the teaching objectives. In the near future, we will require students majoring in chemistry to complete this green experiment and write experimental reports.

■ EXPERIMENTAL TEACHING

The overall objectives for the students are, on the one hand, to conduct transesterification of reused isoamyl acetate and methanol and, on the other, to cultivate their concept of green chemistry and awareness of environmental protection. In the past, when teaching students green chemistry, the examples we gave were remote and difficult for students to understand. The two linked experiments described in this paper provide a good example of using a product from one experiment as a starting material for another experiment and allows students to directly understand the significance of green chemistry through the transesterification experiment.

Because the chemical reagent used throughout the experiment is originally laboratory waste liquid, the amount of raw materials can be further increased. In this way, the problems that students focus on in the experiment are different from those that are at the fore in a microexperiment in conventional teaching. These methods can effectively improve the utilization efficiency of chemical reagents and reduce discharge of waste. About 2 L of isoamyl alcohol can be recycled through this experiment. If all isoamyl acetate in the laboratory is recycled, the consumption of isoamyl alcohol can be decreased by 70%, and more than 500 yuan per year can be saved. This direct profit, in addition to the environmental protection outcome, shows benefits of green chemistry which could encourage students to further their study in this field. Giving students a chance to reduce the waste liquid disposal in the laboratory allows them to realize the significance and necessity of green chemistry in practice, rather than learn it only in theory.

In the experimental class, the transesterification reaction is used to support comparative learning. This experiment is a perfect contrast to the experiment for synthesis of isoamyl acetate, with substantial differences in the experimental principles, operation steps, devices, and types of catalysts used. Students gain a deeper understanding of the knowledge by comparing the two experiments. For example, esterification and transesterification are both reversible reactions, and removing the experimental products from the reaction system is conducive to a positive shift of equilibrium. In the instructional experiment, acetic acid reacts with isoamyl alcohol under the catalysis of sulfuric acid to produce isoamyl acetate and water, and the Dean–Stark apparatus is used to remove the product water from the reaction system to improve the conversion rate. In the transesterification experiment, methyl acetate with a low boiling point was removed from the reaction system by fractional distillation, which promoted the conversion of isoamyl acetate to isoamyl alcohol. The synthesis of isoamyl acetate and transesterification of isoamyl acetate are carried out simultaneously for comparison, so as to give students a more intuitive understanding of the principle of chemical equilibrium and the ability to apply the knowledge to solve practical problems.

■ CONCLUSIONS

The green experiment outlined in this paper uses organic waste liquid to set up experiments with teaching significance and uses the fractionation method to convert isoamyl acetate into isoamyl alcohol. The product can also be reused in the original teaching experiments, so it has good educational and application value. For undergraduates, there is much to learn before they are prepared to protect the environment. They need to receive relevant training at the experimental stage for reduction of chemical laboratory waste liquid discharge and improvement of the use efficiency of organic solutions. This experiment improves material utilization efficiency, makes it easier to understand the principle of product life cycle, and reduces discharge of organic waste liquid. Therefore, we propose it as a beneficial experimental experience for undergraduates.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at https://pubs.acs.org/doi/10.1021/acs.jchemed.1c01027.

Pre-experiment questions and general protocol (PDF, DOCX)

Teaching experimental process for Instructors (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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