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Rapid Transesterification of Aliphatic and Aromatic Esters Using Sodium *Bis*(ethylenedioxy)borate-A Mild Catalyst

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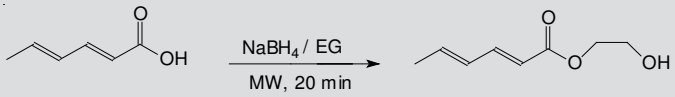
A simple, selective transesterification of aliphatic and aromatic esters using a mild base sodium *bis*(ethylenedioxy)borate is described. The transesterification reactions were performed both in microwave and ultrasonication. Aromatic compounds forms diesters of ethylene glycol while aliphatic compounds forms only monoesters. The IR, MS and NMR characterization are given. In this work, an environmentally benign process for the production of biodiesel from oils using heterogeneous catalyst was developed. Mild borate catalyst was adopted for the production of biodiesel. A study for optimizing the reaction conditions such as the reaction time, the reaction condition, the use of co-solvent and the amount of catalyst, was performed.



Key Words: Selective transesterification, Heterogeneous catalyst, Sodium *bis*(ethylenedioxy)borate, Biodiesel.

INTRODUCTION

Over the last few years, there is an increasing demand for alternative fuels that are environmental friendly especially due to the fact that crude petroleum reserves are dwindling. At present, biodiesel is primarily produced in batch reactors where required energy is provided by heating accompanied by mechanical mixing[1-3]. Alternatively, microwave irradiations and ultrasonic processing is an effective way to attain required heating and mixing while providing the necessary activation energy. Fatty acid esters have assumed importance as research has intensified on the utilization of vegetable oils and animal fats derivatives for liquid fuels, known as biodiesel[4-6]. Trans-esterification is a process used in the production of bio-fuels using vegetable oils. It deals with reaction in which the alcohol reacts with ester by the action of some catalyst to produce different alcohol and different ester wherein the alcohol group of an ester compound is exchanged with another higher alcohol group[7-9]. These reactions are often catalyzed by the action of acid or base.

$$R_1 - OH + RCOOR_2 \longrightarrow R_2 - OH + RCOOR_1$$

The variables affecting the alcoholysis have been intensively investigated as widening industrial uses were found for esters. Molar ratio of alcohol to vegetable oil, type of catalyst, temperature and presence of impurities such as free fatty acids and moisture are few among the variables that have been studied[9-12]. Acids can catalyze the reaction by donating a proton to the carbonyl, thus making it more reactive, while bases can catalyze the reaction by removing a proton from the alcohol, thus making it more reactive[13]. In line with above facts, a new attempt was made to perform *trans*-esterification of aromatic and aliphatic acid esters using borate complex formed out of reaction of sodium borohydride and ethylene glycol under microwave and ultrasonication conditions[13-15]. The reaction was found simpler and faster as compared with other conditions. This report summarises the *trans*-esterification reactions of various aliphatic and aromatic acid esters with the use of borate complexed mild basic catalyst.

EXPERIMENTAL

The catalyst is prepared by *in situ* reaction. All chemicals were purchased from Sigma Aldrich, Germany and used as such. Microwave oven used was BIOTAGE, Intiator 2.5, time; 20 min, solvent; ethyl glycol (10 mL), temperature; 120 ºC. Ultrasonicator from ENERTECH electronics was used for the reactions. Precoated thin layer chromatography plates (E-Merck, Germany, Keiselgel 60, F_{254} 0.2 mm thickness, coated on aluminium sheets) were used for both chemical investigation and bioassays. Column chromatography was performed using silica gel (60-120 mesh). *n*-Hexane and ethyl acetate

were used for elution. NMR spectra were recorded on a Bruker 500 MHz instrument using TMS as the internal standard for both ^1H and ^{13}C NMR experiments. CD_3OD was used as the solvent. Chemical shifts are given in terms of parts per million (δ scale). FTIR was recorded using Bruker (ALPHA) instrument. Mass spectrometry was performed in JEOL GC mate in IITM.

10 mmol of sodium borohydride added to the reaction flask containing 10 mmol of aliphatic acid/aromatic acid ester. Ethylene glycol (5.5 mL) is added slowly at room temperature. The reaction is vigorous with the evolution of hydrogen. After the effervescence ceases, the reaction mixture is placed in micro-oven with the medium low set conditions. The reaction progress is monitored by TLC (60/120) mesh with a suitable mobile phase system. The reaction is completed after 20 min and the mixture is neutralized with the addition of dilute HCl and quenched in water to remove the salts. The product is then extracted in to ethyl acetate and the organic layer is separated and dried over anhydrous sodium sulphate. Then the dried organic layer is concentrated and the product is purified using a column technique. The same reaction was performed in ultrasonicator with the *in situ* generation of the catalyst. The purified product is characterizated by spectroscopic techniques like IR, mass, ^1H and ^{13}C NMR . Table-1 gives the list of various substrates and their corresponding transesterified products.

TABLE-1
LIST OF VARIOUS SUBSTRATES AND THEIR CORRESPONDING TRANS ESTERIFIED PRODUCTS

Comp. No.	Starting material	Product
1	Ethyl benzoate	Ethane-1,2-diyl dibenzoate (EGEB)
2	Methyl ester of palmitic acid	2-Hydroxyethyl hexadecanoate (EGPA)
3	Methyl ester of myristic acid	2-Hydroxyethyl tetradecanoate (EGMA)
4	Methyl ester of stearic acid	2-Hydroxyethyl octadecanoate (EGST)
5	Methyl sorbate	2-Hydroxyethyl(2E,4E)hex-2,4-decanoate (EGSO)
6	6-methyl, methyl nicotinate	2-{[(2-Methylpyridin-4-yl) carbonyl]oxy}ethyl 6-methyl pyridine-3-carboxylate(EGMN)
7	Methyl salicylate	Ethane-1,2-diyl *bis*(2-hydroxybenzoate) (EGSA)
8	Methyl Benzoate	Ethane-1,2-diyl dibenzoate (EGMB)
9	Methyl ester of *trans*-2-hexanoic acid	2-Hydroxyethyl(3E)hex-3-enoate (EGHA)

Compound 1: ^{13}C NMR (CH_3OH-d_4) δ ppm: δ 185.3, 129.7, 130.50, 133.15, 62.74, ^1H NMR (CH_3OH-d_4) δ ppm: 8.01, 8.02, 7.23, 7.14, 8.17, 4.34 ($M^+ + 1$) = 272.7.

Compound 2: ^{13}C NMR (CH_3OH-d_4) δ ppm: 173.1, 66.9, 60.3, 33.9, 31.9, 29.7, 29.4, 29.1, 25.1, 22.8, 14.1, ^1H NMR (CH_3OH-d_4) δ ppm: 0.92, 1. 14, 5.12, 3.67, 4.12 M^+ = 300.7.

Compound 3: ^{13}C NMR (CH_3OH-d_4) δ ppm: 173.1, 66.9, 60.3, 33.9, 31.9, 29.7, 29.4, 29.1, 25.1, 22.8, 14.1, ^1H NMR (CH_3OH-d_4) δ ppm: 1.63, 1.23, 0.93, 3.43, 3.51, 4.45 M^+ = 272.4.

Compound 4: ^{13}C NMR (CH_3OH-d_4) δ ppm: 173.1, 66.9, 60.3, 33.9, 31.9, 29.7, 29.4, 29.1, 25.1, 22.8, 14.1, ^1H NMR (CH_3OH-d_4) δ ppm: 0.93, 1.3, 1.09, 1.13, 1.34, 3.45, 3.6, 4.09 M^+ = 328.5.

Compound 5: ^{13}C NMR (CH_3OH-d_4) δ ppm: 166.5, 144.4, 130.4, 130.3, 118.2, 67.0, 60.4, 19.3, ^1H NMR (CH_3OH-d_4) δ ppm: 1.3, 1.09, 1.13, 3.45, 3.6, 4.09, 5.62, 5.72, M^+ = 156.2.

Compound 6: ^{13}C NMR (CH_3OH-d_4) δ ppm: 166.0, 159.9, 150.0, 135.6, 122.6, 122.4, 63.6,24.8, ^1H NMR (CH_3OH-d_4) δ ppm: 8.74, 8.10, 7.92, 7.90, 4.37 M^+ = 301.3.

Compound 7: ^{13}C NMR (CH_3OH-d_4) δ ppm: 166.0, 161.8, 134.5, 131.3, 121.3, 115.8, 115.3, 63.2, ^1H NMR (CH_3OH-d_4) δ ppm: 7.97, 7.37, 7.47, 4.71, M^+ = 302.3.

Compound 8: ^{13}C NMR (CH_3OH-d_4) δ ppm: 186, 133.1, 128.7, 129.9 63.2, ^1H NMR (CH_3OH-d_4) δ ppm: 7.97, 7.37, 7.47, 4.71($M^+ + 1$) = 272.3.

Compound 9: ^{13}C NMR (CH_3OH-d_4) δ ppm: 168.1, 128.9, 128.0, 88.3, 67.0, 60.3, 26.2, 14.3, ^1H NMR (CH_3OH-d_4) δ ppm: 0.96, 3.45, 3.6, 5.62, 5.72, M^+ = 158.2.

RESULTS AND DISCUSSION

The use of various catalysts in transesterification reactions for the synthesis of biofuels and bioactive lipids was reviewed and the limitations involved in all these catalysts were thoroughly understood. As a part of improvement in this area of work, a new catalyst was developed to study the reduction properties in comparison with other known catalysts. When sodium borohydride was added to ethylene glycol, a brisk effervescence was observed with faster evolution of hydrogen. This prompted to study the reaction kinetics of reduction reactions of both aliphatic and aromatic carboxylic acids by sodium borohydride in ethylene glycol. Reactions were performed by keeping the samples in Microwave oven and the reaction progress was monitored by TLC technique. However it was observed that there was no reduction taking place. On the other hand, when these acids were esterified with methanol and the corresponding esters were reacted with the mixture of sodium borohydride and ethylene glycol, transesterification reaction was taking place resulting in corresponding ethylene glycol esters. When aliphatic acid esters were reacted, transesterification was occurring at one end of ethylene glycol leading to monoester. In case of aromatic acid esters, transesterification was taking place at both the ends of ethylene glycol leading to diester. These products were characterized with spectral studies to confirm the type of esters formed. This can be explained by the following mechanism.

Proposed mechanism for the transesterification reaction: The probable mechanism of the borate catalyzed transesterified reaction is likely to occur in the following path.

Generation of base

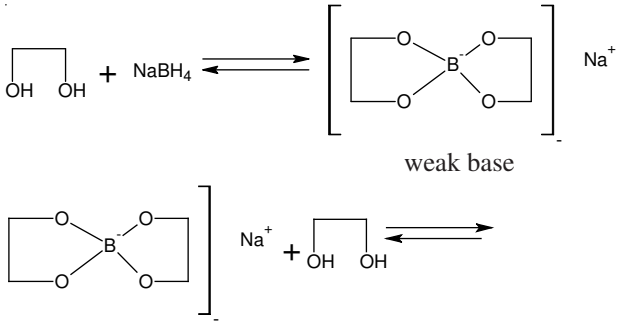
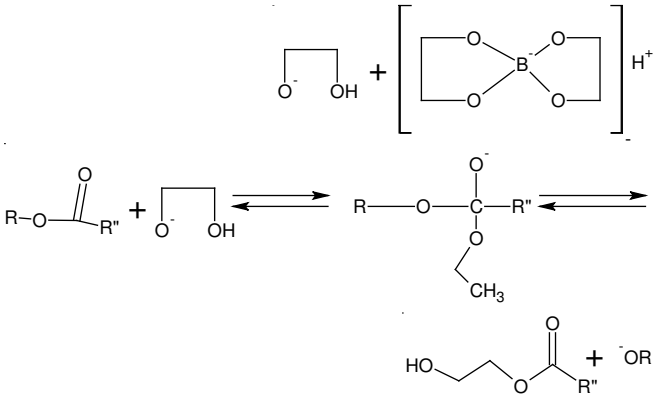


TABLE-2
RATE OF PRODUCT FORMATION UNDER MICROWAVE AND ULTRASONICATION CONDITIONS

Time (min)	Rate of conversion of product in percentage					
	1 equivalent of catalyst		0.1 equivalent of catalyst		0.025 equivalent of catalyst	
	Microwave	Ultrasound	Microwave	Ultrasound	Microwave	Ultrasound
5	56	44	54	42	55	43
10	68	55	70	55	67	55
15	89	69	87	68	88	67
20	99	87	100	88	98	88
25	100	98	100	96	100	97
30	100	100	100	100	100	100



R = Long chain aliphatic group, R" = methyl group.

In transesterification of aromatic substrates, there is a chance of deprotonation and formation of anion which can lead to the diester. In the case of aliphatic substrates this anion is highly unstable because of electron withdrawing aliphatic group and formation of this anion is difficult. In the case of aromatic substrates, this anion is stabilized by electron withdrawing phenyl group and formation of this anion is possible and there by the diester.

Table-2 summarizes the transesterification experiments conducted using ethyl benzoate as the substrate with varying quantities of sodium borohydride and the rate of product formation both under microwave and ultrasonication conditions.

Thus the reaction is independent of the concentration of the catalyst that is recycled after the reaction.

Conclusion

It is concluded that the newly developed catalyst namely, sodium *bis*[ethylene dioxy]borate is mild and more selective as compared with other catalysts used in these reactions. Use of microwave conditions for these reactions enhances the rapid conversion as compared with other conditions. Also the reaction is more selective and eco-friendly resulting in higher rate of conversion with less environmental hazards. It is one of the best catalysts for the synthesis of biofuels and bioactive lipids under microwave conditions.

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