



Microwave assisted process intensification of lipase catalyzed transesterification of 1,2 propanediol with dimethyl carbonate for the green synthesis of propylene carbonate: Novelties of kinetics and mechanism of consecutive reactions



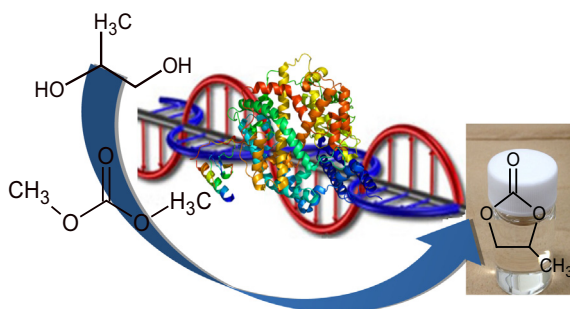
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HIGHLIGHTS

- Synthesis of propylene carbonate from 1,2-propanediol and dimethyl carbonate is presented as a green route.
- Synergism of lipase catalysis and microwave irradiation is achieved.
- Novelty of kinetic modeling for consecutive reactions is reported for the first time.
- 92.4% conversion of the product under microwave as compared to 54% under conventional heating in 5 h.
- Environmentally benign route of cyclic carbonate synthesis under non aqueous media.

GRAPHICAL ABSTRACT



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ABSTRACT

Green chemistry inherently hinges on process intensification through catalysis and waste minimization. The synergism of enzyme catalysis with microwave irradiation was studied systematically in this work for a consecutive reaction about which no literature report exists. Transesterification reaction of renewable starting materials (1,2 propanediol and dimethyl carbonate) was studied as a new strategy for environmentally benign route of cyclic carbonate synthesis in non aqueous media. A variety of supported enzymes were considered including Lipozyme RM IM, Lipozyme TL IM, Amano and *Candida antarctica* (Novozyme 435) among which Novozym 435 was the best. Both reactions occur under the influence of enzyme and also are enhanced by microwave irradiation. Thus, the example reported here serves as the first of its kind. The studies cover influence of different process parameters on reaction rate and selectivity of propylene carbonate and include agitation speed, solvent, loading of catalyst, reactant concentration (mole ratio) and temperature. A novel kinetic model was developed by finding forward and backward reaction rate constants for each step of the reaction. Microwave irradiation not only increases reaction rate but also improves the thermal stability of enzyme. Maximum conversion of 93% was obtained in 6 h using 250 mg of enzyme loading with 1 and 3 mmol of 1,2 propanediol and dimethyl carbonate in 15 mL solution made up with 1,4-dioxane as solvent at 70 °C as compared to 54.4% conversion under conventional heating, thus proving the synergism between microwave irradiation and lipase. The enzyme is reusable and the results are novel.

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Nomenclature

A	reactant species A, propylene glycol	k_{12}	chemisorption rate constant for forward reaction BEz to BAEz
B	reactant species B, dimethyl carbonate	k'_{12}	chemisorption rate constant for backward reaction BAEz to BEz
Ez	Enzyme site	k_{21}	chemisorption rate constant for forward reaction BAEz to CEz
BEz	Adsorbed B on enzyme site	k'_{21}	chemisorption rate constant for backward reaction CEz to BAEz
C	2-hydroxypropyl methyl carbonate	k_2	chemisorption rate constant for forward reaction BEz to CEz
D	4-methyl-1,3-dioxolan-2-one	k'_2	chemisorption rate constant for backward reaction CEz to BEz
BAEz	Intermediate adsorbed on enzyme Ez	k_3	chemisorption rate constant for forward reaction CEz to D
CEz	Intermediate C adsorbed on enzyme Ez	E_1	activation energy of forward reaction (B to BEz)
C_A	concentration of A, (mol/L)	E'_1	activation energy of backward reaction (B to BEz)
C_B	concentration of B, (mol/L)	E_2	activation energy of forward reaction (BEz to CEz)
C_{BEz}	concentration of B at enzyme surface	E'_2	activation energy of backward reaction (BEz to CEz)
C_{BAEz}	concentration of intermediate BA at enzyme surface	E_3	activation energy of forward reaction (CEz to D)
C_{CEz}	concentration of C at enzyme surface		
C_D	concentration of D, (mol/L)		
C_M	concentration of methanol M, (mol/L)		
C_{Ez}	concentration of vacant enzymatic sites		
C_{Et}	total concentration of the enzymatic sites		
k_1	chemisorption rate constant for forward reaction B to BEz		
k'_1	chemisorption rate constant for backward reaction B to BEz		

1. Introduction

A considerable attention is focused on to the synthesis of polymers having 5-membered cyclic carbonates which are employed in a number of commercial utilities. The cyclic carbonate group may be attached to the polymer backbone or suspended from the polymer chain. Oligomers with terminal cyclic carbonate moieties can be synthesized from epoxy resins [1,2].

Propylene carbonate (PC) is a versatile chemical which is used for making polycarbonate resins, as an electrolyte for lithium batteries, fuel additive, precursor for a variety of fine chemicals and inert solvent. PC is found to be useful for the separation of CO₂ and H₂S [3,4]. Propylene carbonate is a polar, aprotic, nontoxic, and biodegradable solvent. PC has excellent solvency with high boiling as well as flash point and low odor levels. Furthermore, the use of PC as a solvent has increased significantly in the past few years for removing paint, greases and for cleaning surfaces. Therefore, cyclic carbonates are viewed as ecofriendly alternate solvents. Several methods have been reported to synthesize five-membered cyclic carbonates. These carbonates are used in a number of metal-catalyzed reactions such as alkene metathesis, carbonylation, hydroxylation, Sonogashira coupling, enantioselective hydrogenation, oxidation, allylic alkylation and Heck vinylation [5–14].

Propylene or cyclic carbonates have been synthesized reacting 1,2-propanediol and phosgene or alkyl carbonate [15,16] and reaction of oxiranes with alkali metal carbonates [17]. A number of recent publications report synthesis of cyclic carbonates using transesterification of 1,2-glycols with ethylene carbonate [18], 1,2-propanediol and urea [19], oxirane and CO₂ [20], oxirane and 2-butyrolactone [21], ketal from a 1,2-glycol and cyclohexanone in supercritical CO₂ medium [22]. The major drawbacks of some of these reactions are due to their environmental hazard and lack of economic viability due to low conversion and yield. Cyclic carbonates are conventionally synthesized using cumbersome routes resulting into low yields; for instance, reaction of trimethylolpropane and pentaerythritol followed by thermal disproportionation of products and distillative depolymerization, under sub-atmospheric pressure above 200 °C [23].

Polyester synthesis using lipase catalysis is a green chemistry approach since it is conducted under mild conditions with accurate

control of regio, chemo-, and enantio-selectivity. Lipase catalysts can be effectively used in non-aqueous conditions. Lipase catalyzed synthesis of polyesters has been attempted using polycondensation of diacids/esters and diols, and self polycondensation of oxyacids/esters, and polymerization of lactones through ring opening [24].

Six-membered cyclic-carbonates have been synthesized using lipase [25] wherein tri-methylene carbonate (TMC), a typical biodegradable synthetic plastic was synthesized using dimethyl carbonate (DMC) and 1,3 diol. *Candida antarctica* lipase showed the highest TMC yield with maximum of 63% at 70 °C for 6-day reaction in an organic solvent and typical ring opening polymerization of TMC was accomplished with highest conversion of 91% at 100 °C in 5 days. Six-membered cyclic carbonates (~85% yield) were synthesized using lipase-catalyzed reaction of TMP with dialkylcarbonate followed by non-catalytic thermal disproportionation under solventless conditions at 80 °C giving a mixture of cyclic and linear carbonates [26]. Reaction between polyol and dialkylcarbonate over Novozym 435 under different conditions has been reported [27]. Synthesis of glycerol carbonate from glycerol and dimethyl carbonate in THF has been achieved using lipase catalysis at 60 °C for 30 h [28]. All these above mentioned methods have demerits of long reaction times and low conversions. This issue is addressed in the current research work by carrying out the reactions under microwave irradiation including kinetic modeling.

The effect of microwave irradiation on bio-systems has interesting outcomes. For instance, the effect of microwave irradiated lipase-catalyzed reactions has earlier been tried out to witness rate enhancement [29–37]. It has been found that Microwave irradiation has practically no effect on activation energy or has only moderate effect in a few cases, but it provides enough excitation to overcome the energy barrier. It leads to completion of the reaction more quickly than the conventional heating. The absorption of energy causes the functional groups involved in reaction to have higher reactivity with surrounding reactant than they are simply incubated at the same temperature. The two important factors have significant contribution on effect of microwave in enzyme catalysts: (i) di-electric property, and (ii) polarity of reaction medium. Microwave irradiation also assists in improving thermal

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