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 Cite this: *RSC Adv.*, 2015, 5, 30005

Reaction routes in catalytic reforming of poly(3-hydroxybutyrate) into renewable hydrocarbon oil†

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Poly(3-hydroxybutyrate) or PHB is an energy storage material of microbial organisms and can be reformed into hydrocarbon oils rich with aromatic compounds. This work investigated the main reaction routes from PHB to the key intermediates and final hydrocarbons. The main sequential reactions under catalysis of phosphoric acid at moderate temperatures (200–230 °C) consist of: (1) decomposition of PHB into crotonic acid, a major monomeric intermediate, (2) deoxygenation of crotonic acid, and (3) combination of the deoxygenated molecules. The oxygen in PHB is removed as CO₂ and H₂O in stage (2), involving decarboxylation and ketonization of crotonic acid. The main aromatic compounds are formed in stage (3) from propylene and 2,3-dimethyl-2-cyclopenten-1-one as two key intermediates, the former from decarboxylation and the latter from ketonization of crotonic acid. The reaction routes reveal that the formation of aromatics is affected to a great extent by the concentrations of phosphoric acid and water in the reaction, which can be used to control the composition of hydrocarbon oil.

 Received 19th February 2015
Accepted 12th March 2015

DOI: 10.1039/c5ra03195h

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1 Introduction

Transportation fuels derived from biomass could reduce fossil fuel consumption and CO₂ emission since the renewable feedstock originates from CO₂, water and sunlight. Because of the high oxygen content of biomass, however, bio-based fuels such as ethanol (C₂H₆O) contain a substantial amount of oxygen which not only reduces the fuel's energy content but also requires advanced engine technologies.¹ Bio-based drop-in gasoline that has the same chemical composition of the petrochemical counterpart could solve the problem, but presents technical challenges to refineries including: deoxygenation of biofuel to a desired low oxygen content and reforming of the chemical structure of hydrocarbons for high antiknock quality (high octane number). In general, straight-chain paraffins are more prone to knocking than branched-chain paraffins, olefins and cyclic hydrocarbons. Likewise, cycloparaffins are more knock-prone than aromatics. To satisfy modern high performance automotive engines, for example, unleaded gasoline contains a substantial amount (maximum 35 vol%) of aromatics that replace lead-containing additives and sustain a high octane number.² Conventional thermochemical processing of biomass may produce a drop-in fuel, but needs multiple catalytic reactions and consumes a large amount of hydrogen.³ Besides, the thermochemical process conditions are very much

dependent on the composition of biomass feedstock which varies with season and location.

Poly(3-hydroxybutyrate), PHB (C₄H₆O₂)_n (*n* = 6000–12 000) is an energy storage material of many microbial species and can be produced through fermentation of renewable carbohydrates or CO₂/H₂.⁴ Recently, we reported a simple one-pot conversion of PHB into hydrocarbon oil from which a gasoline-like drop-in fuel was obtained through conventional distillation. In the reaction catalyzed with H₃PO₄, PHB was completely converted and deoxygenated to a great extent with formation of CO₂ and propylene (C₃H₆), and more interestingly with formation of substantial amount of aromatic compounds.⁵ We found that crotonic acid (CA, *trans*-2 butenoic acid, C₄H₆O₂), was a key monomeric intermediate in the early stage of PHB conversion. Under typical reaction conditions (100% H₃PO₄ solution, 220 °C and 3 hours), CA was completely converted and 90.9% of the original carbon was recovered from the gas and liquid products.⁵ We, however, had little knowledge on how CA was deoxygenated and how aromatic rings were formed under the reaction conditions. Compared to the conventional biomass feedstock, PHB is a simple consistent raw material and can be conveniently converted into drop-in fuels or aromatics that can be blended with conventional bio-fuels such as ethanol and fatty acids methyl ester to improve the quality of biofuels. The reaction mechanism of PHB reforming, especially the decarboxylation of CA and formation of aromatic compounds, would help us understand and control the new reaction system. In this work, we explored the reaction routes from PHB to the key intermediates and major final hydrocarbons.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ra03195h

2 Experimental section

2.1 Materials

Crotonic acid (CA, 98%), 2,3-dimethyl-2-cyclopenten-1-one (99%), 3-methyl-2-cyclohexenone (>98%), 3-butenic acid (97%), 3-hydroxybutyric acid (3HB, 98%), toluene (99.8%) and polyphosphoric acid (115% H₃PO₄ basis) were purchased from Sigma-Aldrich (St Louis, MO, USA). Butyric acid (99%) was obtained from Alfa Aesar (MA, USA). Solutions of phosphoric acid (50% to 100% H₃PO₄) were prepared from polyphosphoric acid and distilled de-ionized water. Poly(3-hydroxybutyrate) (PHB, 98%) was obtained from Bio-on (Bologna, Italy). Its weight-average molecular weight (138 000 Da) and number-average molecular weight (53 100 Da) were measured with gel permeation chromatography (GPC) and calibrated with polystyrene standards. The polystyrene standards with narrow molecular weight distribution were purchased from Sigma-Aldrich.

2.2 Liquid products formation and analysis

In oil-producing experiments, a pre-determined amount (0.5–1 g) of reagents (PHB, CA, 3HB) and 10 mL of H₃PO₄ solutions were put into a 20 mL polytetrafluoroethylene (PTFE) reactor, and the reactor was purged with N₂ for about 10 minutes. The PTFE reactor was then sealed and left for a predetermined reaction time in a thermostat oven that was maintained at a desired temperature (165 to 240 °C). After reaction, the PTFE reactor was quickly cooled down under tap water. The reaction under the conditions of 100% H₃PO₄ solution at 230 °C for 3 hours is defined as a typical reaction thereafter. In controlled reactions with butyric acid (or 2,3-dimethyl-2-cyclopenten-1-one or 3-methyl-2-cyclohexenone), 1 g of butyric acid (or 2,3-dimethyl-2-cyclopenten-1-one, or 3-methyl-2-cyclohexenone) and 10 mL of 100% H₃PO₄ solution were put into a 20 mL polytetrafluoroethylene (PTFE) reactor, and the reaction was maintained at 230 °C for 3 hours. For the 2-propanol reaction with 2,3-dimethyl-2-cyclopenten-1-one, 0.5 g 2-propanol and 0.3 g 2,3-dimethyl-2-cyclopenten-1-one were put in 10 mL 100% H₃PO₄ at 230 °C for 3 hours. In order to check acylation reaction, toluene (2 g) and CA (0.5 g) were reacted in a solution of 100% H₃PO₄ (0.5 g) at 150 °C for 3 hours.

The liquid products were recovered with methylene chloride and analyzed with a gas chromatograph-mass spectrometer (GC-MS, Bruker 436-GC, USA) equipped with an Rtx-1 capillary column and EI ion source (70 eV). The temperature of the injector was set at 250 °C and the temperature program of the column was started at 30 °C for 10 min, increased to 230 °C at 8 °C min⁻¹ and held for 2 min, and further increased to 260 °C at 10 °C min⁻¹ and held for 10 min. The compounds were identified by using a NIST11 mass spectral data library. The concentrations of organic acids (CA, isocrotonic acid, 3-butenic acid, and 3-hydroxybutyric acid) in H₃PO₄ solutions were determined with a high performance liquid chromatograph (HPLC, Shimadzu, Japan), after the reaction solution was appropriately diluted. The yield of isocrotonic acid was

estimated from the ratio of peak areas of isocrotonic acid to CA multiplied by the yield of CA.

2.3 Gas formation and analysis

In a typical experiment for gas products and analysis, 3.6 g of PHB or crotonic acid and 72 mL of H₃PO₄ solution were added into a 180 mL pyro-beaker, which was put in a 600 mL autoclave (Parr Instrument, IL, USA). The autoclave was purged with nitrogen at least ten times of the reactor volume to remove air. The reactor was then sealed and heated to a pre-determined temperature. When the temperature reached the setting value in about half an hour, the reaction time was set as zero, and thereafter recorded. After reaction, the reactor was cooled down in ambient conditions. The quantitative determination of CO₂ and propylene was performed by using a gas chromatograph equipped with a thermal conductivity detector (GC-TCD, Bruker 450-GC, FL, USA) and a Carboxen-1006 Plot column. Both CO₂ and propylene were calibrated with pure gases against helium.

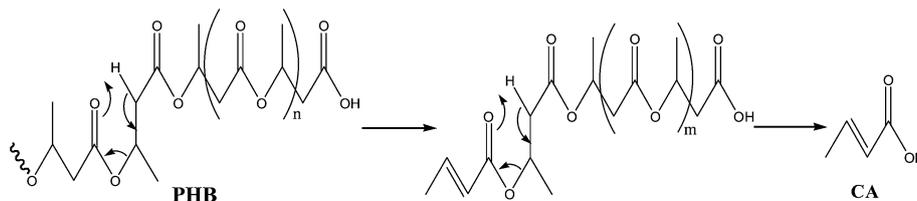
2.4 Reactions of propylene

The reactions of propylene as a sole or co-reagent were conducted in the 600 mL autoclave in which a 180 mL pyro-beaker contained a phosphoric acid solution and co-reagents. After purge with nitrogen, propylene was introduced into the reactor till an initial pressure of 760 kPa. The reaction was conducted at 230 °C for 3 hours. For propylene as the sole reagent, 50 mL of 100% H₃PO₄ was put in the pyro-beaker. For the reactions of propylene with 2,3-dimethyl-2-cyclopenten-1-one (or 3-methyl-2-cyclohexenone), 1 g of 2,3-dimethyl-2-cyclopenten-1-one (or 3-methyl-2-cyclohexenone) and 30 mL of 100% H₃PO₄ were put in the beaker. For the reaction of propylene with toluene, 8 g of toluene and 50 mL of 100% H₃PO₄ were put in the pyro-beaker. After the reactions, the reactor was cooled down in ambient conditions. The liquid products were recovered with methylene chloride for GCMS analysis.

3 Results and discussion

3.1 Monomeric intermediates

CA and 3HB are two possible monomeric intermediates of PHB degradation and their predominance depends on reaction conditions. Under pyrolysis conditions, PHB is primarily decomposed into CA, *via* a β -elimination six-member ring structure (Scheme 1).^{6,7} Under acidic hydrolysis conditions, both 3HB and CA are formed.⁸ The molar ratio of 3HB to CA reflects the relative extent of hydrolysis *versus* pyrolysis of PHB. As shown in Table 1, the molar ratio of CA to 3HB in the reaction solutions (50–70% H₃PO₄) at 220 °C is much lower than that in the pyrolysis of PHB. It indicates that the acidic hydrolysis, instead of the β -elimination six-member ring structure could be the main route of PHB degradation in the H₃PO₄ solutions. The double bond of CA may be formed from dehydration of 3HB *via* β -elimination.⁶ Table 1 also shows that 3HB dehydration was promoted with increase of H₃PO₄ concentration and temperature. In a solution of 100% H₃PO₄, CA was the dominant monomeric product even at relative low temperatures (165–



Scheme 1 CA formation *via* six-membered ring state of PHB in pyrolysis condition.^{6,7}

Table 1 The yields of monomeric products from PHB degradation under different reaction conditions

H ₃ PO ₄ (%)	Temperature (°C)	Time (h)	3HB (wt%)	CA (wt%)	CA/3HB (mol/mol)
100	165	3	2.9	28.8	12.0
100	180	3	0.2	3.4	20.6
100	220	3	ng ^a	ng	—
100	220	1	ng	1.3	—
85	220	3	ng	ng	—
85	210	3	0.3	0.2	0.8
70	220	3	11.2	3.7	0.4
50	220	3	72.6	12.0	0.2

^a ng = negligible.

180 °C). In a reaction under the conditions of 100% H₃PO₄ at 220 °C for 3 hours, both CA and 3HB were completely converted into gas and liquid products. In the following experiments, the typical reaction conditions (100% H₃PO₄, 230 °C and 3 hours) were used for analysis of final products. We also used mild reaction conditions (*e.g.*, 85% H₃PO₄, 230 °C and 1 hour) to find the key intermediates that might appear in the early stage of the reaction. Fig. 1 reveals an interesting fact with GCMS analysis that PHB, CA and 3HB, when they were used as the initial reagent, were converted into the same final products under the typical reaction conditions. Fig. 1C1 and C2 reveal that CA was the main intermediate of 3HB conversion and observed only in the early stage under the mild reaction conditions. Under the typical reaction conditions, some 3HB might be formed initially, but quickly converted into CA and further to final hydrocarbons. Our previous work also revealed that the same gas products were formed from PHB and CA.⁵ Based on these facts, it was concluded that CA was the key monomeric intermediate in PHB reforming. In the following experiments, either PHB or CA was used as the reagent to find the intermediates and mechanisms of the reactions following PHB degradation.

3.2 Final gas and liquid products

We first check the final gas and liquid products under different reaction conditions. It was found that PHB and CA were to a great extent deoxygenated with CO₂ and propylene (C₃H₆) being the major products in the gas phase (Table 2) and aromatic compounds (alkylbenzenes and naphthalenes) being the major compounds in the liquid oil (Table 3). Specifically, the chemical composition of liquid oil changed depending on the reaction conditions such as reaction temperature, time, and the concentration of H₃PO₄ (Table 3). Four major compounds were

identified with GCMS analysis as shown in Fig. 1A. They are 1,2,3,4-tetramethyl-5-(1-methylethyl)-benzene (compound 1 thereafter), 1,2,3,4-tetramethylbenzene (compound 2 thereafter), 1,2,3,5-tetramethylbenzene (compound 3 thereafter), and 1-indanone,3,3,4,5,7-pentamethyl-benzene (compound 4 thereafter). In the typical reaction, compound 1 is the predominant compound of hydrocarbon oil and has a similar chemical structure of compounds 2 and 3, probably involving the same reaction intermediate and mechanism.

3.3 Crotonic acid decarboxylation and propylene formation

Deoxygenation of PHB occurs *via* CA decarboxylation because CO₂ and propylene are the predominant gaseous products under different reaction conditions as shown in Table 2. The mole and weight yields of CO₂ and propylene from PHB are provided for comparison. Since little CO was detected in the gas phase, decarbonylation of PHB or CA was negligible and not considered in this study. According to the stoichiometry of CA decarboxylation (C₄H₆O₂ → C₃H₆ + CO₂), equal molar concentrations of propylene and CO₂ were expected, but the actual molar ratio of CO₂ to C₃H₆ ranged from 5.5 to 17.1, depending on the reaction conditions. It might be attributed to further conversion of propylene into final products, but also to other reaction routes in which CO₂ is formed with little propylene being formed.

Early studies have pointed out that decarboxylation of CA occurs primarily *via* a six-member ring transition state (Scheme 2) in which CA was first converted to 3-butenic acid.^{9,10} It has also been reported that isocrotonic acid is an essential intermediate in formation of 3-butenic acid, a precursor to the six-member ring structure intermediate.⁹ Very interestingly, both isocrotonic acid and 3-butenic acid were detected, especially in

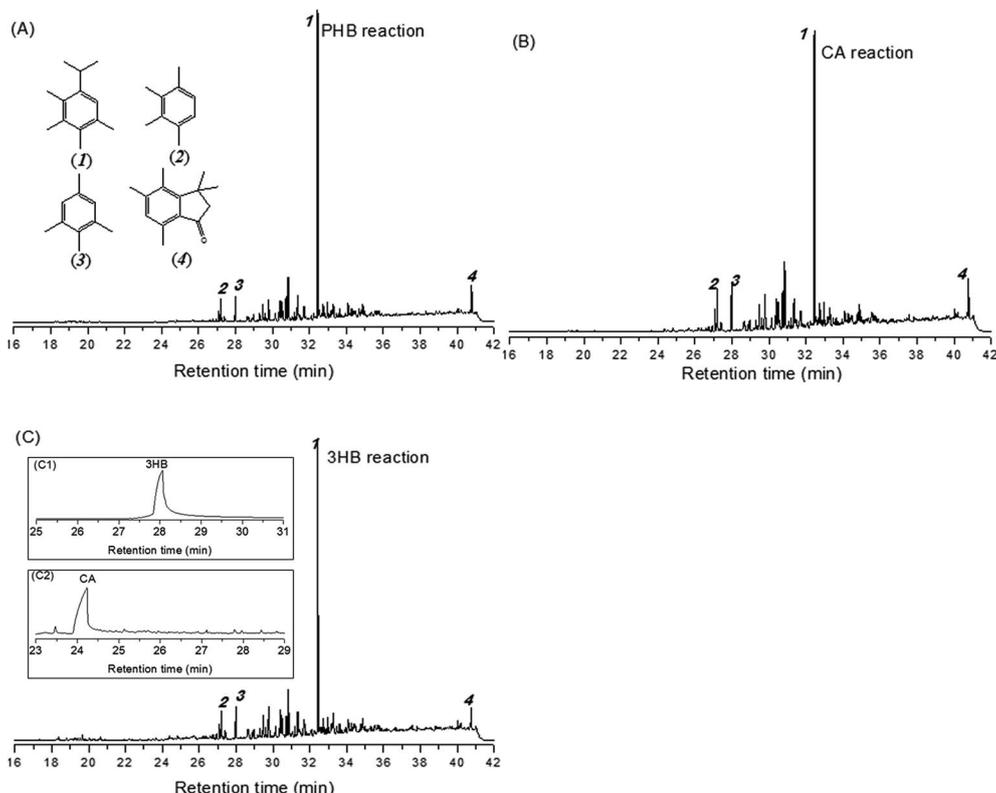


Fig. 1 GCMS spectra of hydrocarbon oils and the chemical structures of compounds 1–4. (A) Spectrum of hydrocarbon oil from PHB in the typical reaction conditions (100% H_3PO_4 , 230 °C, 3 hours); (B) spectrum of hydrocarbon oil from CA in the typical reaction conditions; (C) spectrum of hydrocarbon oil from 3HB in the typical reaction conditions; (C1) spectrum of pure 3HB; (C2) spectrum of the reaction products in the initial stage of 3HB conversion (85% H_3PO_4 , 230 °C, 1 hour).

Table 2 The yields of CO_2 and propylene from PHB under different reaction conditions

H_3PO_4 (%)	Temperature (°C)	Time (h)	CO_2 (wt%)	$^a\text{CO}_2$ (mol%)	Propylene (wt%)	$^a\text{Propylene}$ (mol%)	$\text{CO}_2/\text{propylene}$ (mol/mol)
70%	220	1	25.9	50.7	4.5	9.2	5.5
100%	220	1	33.2	65.0	2.4	4.9	13.3
115%	220	1	19.9	38.9	1.4	2.9	13.4
100	220	3	35.3	69.1	2.5	5.1	13.5
100	220	6	38.5	75.3	2.6	5.3	14.2
100	165	3	12.6	24.7	1.1	2.3	10.7
100	195	3	32.4	63.4	1.8	3.7	17.1
100	240	3	38.2	74.7	2.9	5.9	12.7

^a The molar yields of CO_2 and propylene are based on the equivalent moles of CA in PHB.

the early stage of the reaction (Table 4). Based on the information above, a reaction route is suggested for PHB decarboxylation *via* CA (Scheme 1 and 2). It should be pointed out that the reactions in Scheme 2 can also occur at high temperatures (*e.g.*, 320 °C) in the absence of H_3PO_4 ,⁹ but proceed quickly at much lower temperatures (200–240 °C) with the acid catalysis. Most likely, the isomerization of CA to 3-butenic acid in this work is promoted by protons, because isomerization involves electron transfer. In the absence of H_3PO_4 solution, 3-butenic acid was not found in the same reaction conditions (Table 4).

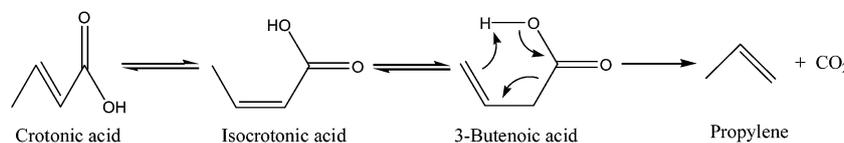
3.4 Propylene oligomerization and alkylation

In contrast to inert CO_2 , propylene is an active reagent under the reaction conditions and participates in formation of other chemicals in hydrocarbon oil. In a controlled experiment with propylene being the sole reagent, propylene was oligomerized to C_6 – C_{12} alkenes determined with GCMS analysis (Fig. 2B), but no aromatic compounds were formed. Interestingly, these alkenes from propylene are quite similar to the alkenes obtained from PHB reaction (Fig. 2A). This fact implies that the high content of

Table 3 Influence of reaction conditions on chemical composition of liquid oil from CA reaction^a

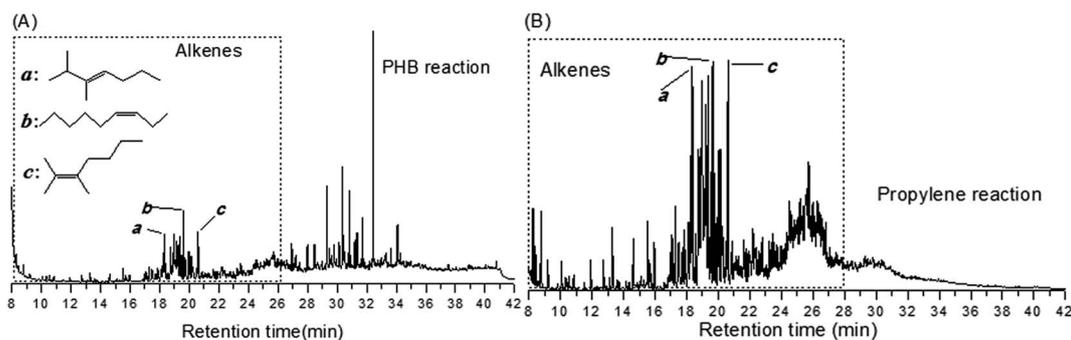
Reaction conditions			O-containing compounds			Hydrocarbon compounds		
H ₃ PO ₄ (%)	Temperature (°C)	Time (h)	Ketones (%)	Others ^b (%)	Alkenes (%)	Cyclic ^c	Benzenes (%)	Naphthalenes (%)
85	230	3	12.6	ng ^d	51.1	5.3	30.6	ng
100	230	0.5	15.5	39.7	ng	4.8	40.0	ng
100	230	3	5.5	1.0	1.6	3.8	78.8	9.3
100	210	3	16.0	0.4	1.4	3.4	72.4	6.4
100	180	3	22.5	0.3	1.0	5.1	70.6	0.6

^a The percentage composition is based on the relative peak area in the GCMS analysis. ^b The others include organic acids and esters, etc. ^c The cyclic hydrocarbons did not include the aromatics. ^d ng = negligible.

**Scheme 2** The proposed decarboxylation mechanism for propylene production.^{9,10}**Table 4** Yields of intermediates in the early stage of CA decarboxylation in H₃PO₄ solutions at 230 °C for 30 min

Solution	3-Butenoic acid (3BA) (mol%)	Isocrotonic acid (IA) (mol%)	Remaining CA (mol%)	3BA : IA : CA (mole ratio)
100% H ₃ PO ₄	0.7	2.1	34.7	1 : 2.3 : 49.6
85% H ₃ PO ₄	1.7	3.8	47.4	1 : 2.2 : 27.9
None ^a	Not detected	2.9	94.5	—

^a Pyrolysis of CA in the absence of phosphoric acid solution.

**Fig. 2** GCMS spectra of hydrocarbon oils from PHB and propylene reaction. (A) Spectrum of hydrocarbon oil from PHB reaction in 85% H₃PO₄ at 230 °C for 3 hours; (B) spectrum of hydrocarbon oil from propylene reaction in 100% H₃PO₄ at 230 °C for 3 hours.

alkenes formed in low acid solution (85% H₃PO₄, in Table 3) may be attributed to propylene oligomerization. When propylene and toluene were the co-reagents under the same reaction conditions, propylene participated in alkylation with toluene to form several substituted aromatic compounds (Fig. S1†). Obviously, propylene alone cannot form the major aromatic compounds (1–4) in the liquid oil (Fig. 1A). In another word, decarboxylation of CA is not the only reaction route of PHB deoxygenation. There must be other main routes that lead

to formation of major aromatic compounds in the hydrocarbon oil.

3.5 Ketonization of crotonic acid

As shown in Table 3, ketones were formed as the major O-containing compounds from CA under the reaction conditions. Based on our earlier observation that water, in addition to CO₂, was also formed from CA deoxygenation,⁵ ketonization of CA is a possible reaction, in which two molecules of carboxylic

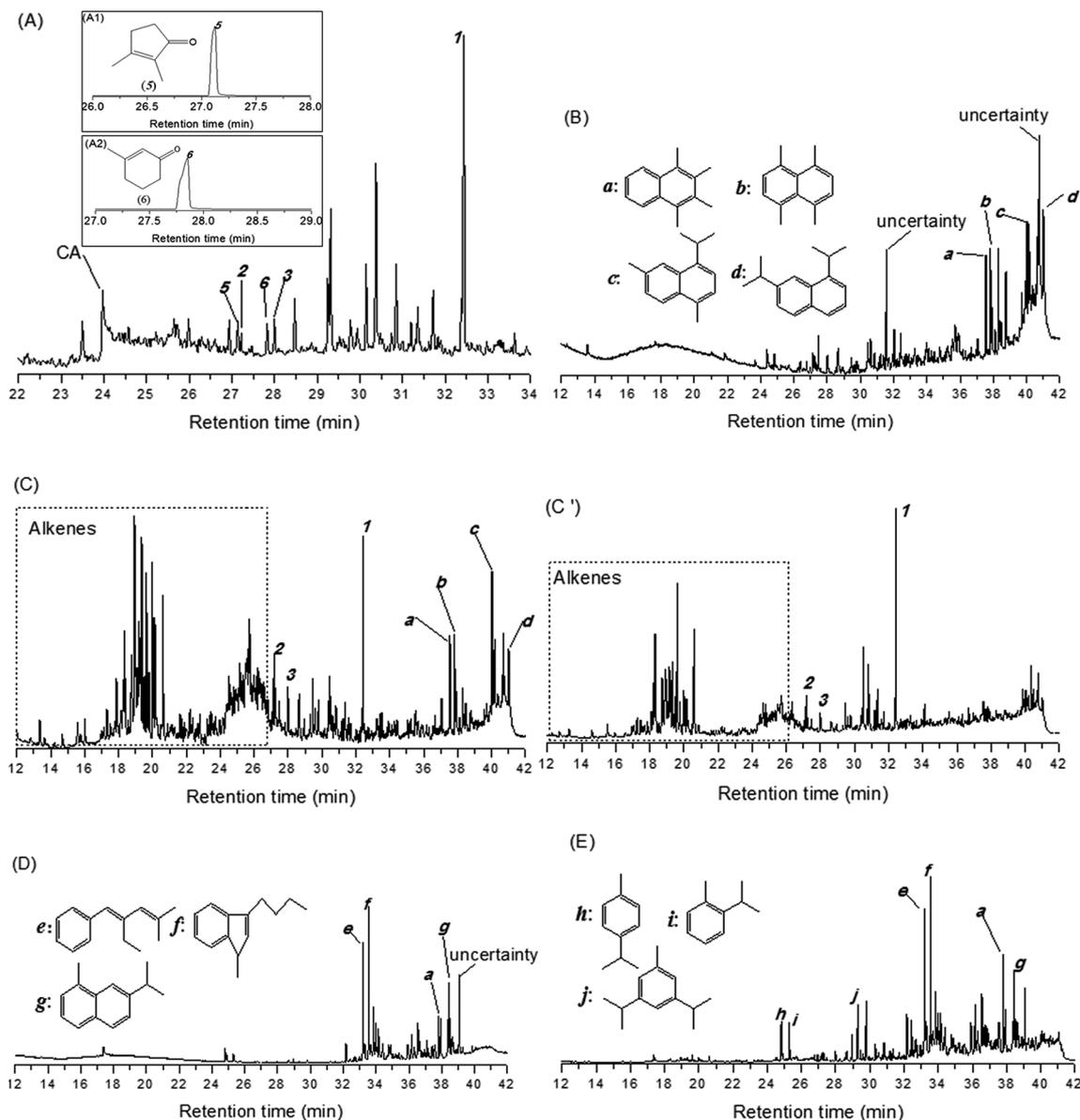
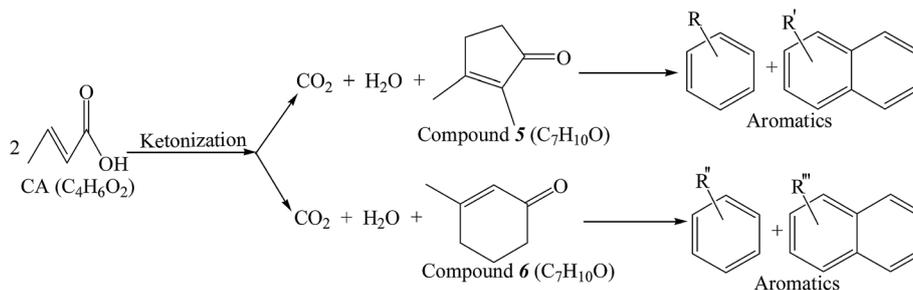


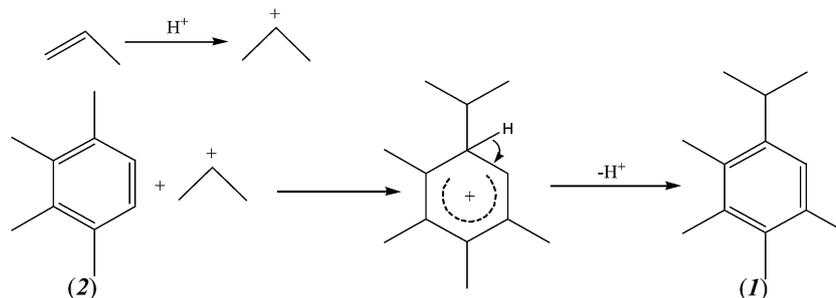
Fig. 3 GCMS spectra of two initial intermediates and their further reaction products. (A) Spectrum of the reaction products in an initial stage of PHB conversion (85% H_3PO_4 , 230 °C, 1 hour); (A1) spectrum of 2,3-dimethyl-2-cyclopenten-1-one (5) and its chemical structure; (A2) spectrum of 3-methyl-2-cyclohexen-1-one (6) and its chemical structure; (B) spectrum of oil products from compound 5 reaction in 100% H_3PO_4 at 230 °C for 3 hours; (C) spectrum of oil products from compound 5 reaction with propylene in 100% H_3PO_4 at 230 °C for 3 hours; (C') spectrum of oil products from compound 5 reaction with 2-propanol in 100% H_3PO_4 at 230 °C for 3 hours; (D) spectrum of oil products from compound 6 reaction in 100% H_3PO_4 at 230 °C for 3 hours; (E) spectrum of oil products from compound 6 reaction with propylene in 100% H_3PO_4 at 230 °C for 3 hours.

acids are converted into one ketone, one CO_2 , and one water.¹¹ In an controlled reaction with butyric acid as the reagent, the saturated C_4 organic acid remained largely intact under the typical reaction conditions, except formation of a very small amount of 4-heptanone detected with GCMS (Fig. S2[†]). The mass spectrum of 4-heptanone is compared with a reference spectrum in Fig. S3.[†] The butyric acid reaction reveals two important facts: (1) that the double bond of CA (an unsaturated C_4 acid) plays a determinant role in its conversion under the typical reaction conditions, and (2) that ketonization of organic

acids does occur in the reaction solution. According to the unsaturation degrees of reagents and products, two CAs with total four unsaturation degrees may be ketonized into one $\text{C}_7\text{H}_{10}\text{O}$ compound (three unsaturation degrees), one CO_2 (one unsaturation degree) and one H_2O (zero unsaturation degree). We checked the products distribution in the early stage of CA and PHB reactions in H_3PO_4 solution, and find two unsaturated seven-carbon compounds, 2,3-dimethyl-2-cyclopenten-1-one ($\text{C}_7\text{H}_{10}\text{O}$, compound 5 thereafter) and 3-methyl-2-cyclohexenone ($\text{C}_7\text{H}_{10}\text{O}$, compound 6 thereafter). They were detected with



Scheme 3 The proposed formation and conversion of compounds 5 and 6.



Scheme 4 A proposed alkylation mechanism for the formation of compound 1.

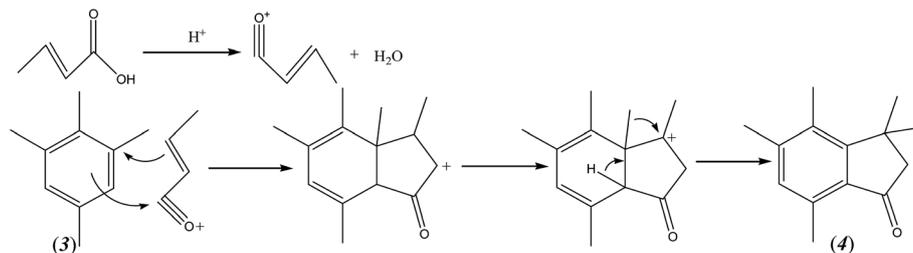
GCMS and confirmed with pure chemicals obtained from Sigma-Aldrich. Their chemical structures are shown in Fig. 3A and mass spectrum in Fig. S3.† Detected only in the early time of CA and PHB reactions, compounds 5 and 6 were active intermediates and further converted to aromatic compounds (benzenes and naphthalenes) which is described in the next subsection. Although the detailed mechanism of compounds 5 and 6 from CA is not clear yet, the presence of these two compounds confirms ketonization of CA (Scheme 3). Importantly, the ketonization reaction provides an alternative route to CO₂ formation with no propylene being formed. It also explains the high molar ratio of CO₂ to propylene mentioned above.

3.6 Formation of main aromatic compounds

Compound 5, one of the detected unsaturated ketones, was found a key intermediate in the formation of main aromatics from CA and PHB. When compound 5 was used as an initial reagent under the typical reaction conditions, the products were much dependent on propylene. In the absence of propylene, naphthalenes (compounds a–d in Fig. 3B) were the main products rather than the main aromatic compounds 1–4 from CA or PHB. In the presence of propylene, however, the main compounds 1–3 were formed as shown in Fig. 3C. Interestingly, some naphthalenes (compounds a–d in Fig. 3B) were also detected in the reaction of compound 5 with propylene. This might be attributed to the fact that compound 5 was dissolved in the H₃PO₄ solution while propylene was in the gas phase. The separation of two reagents favored the formation of naphthalenes. To check this hypothesis, we replaced propylene with 2-propanol in the reaction with compound 5. 2-Propanol was dissolved and mixed with

compound 5 very well in the H₃PO₄ solution, and could be quickly converted to propylene in acid catalytic conditions.¹² Fig. 3C' is the GCMS spectrum of the products formed in the reaction of 2-propane with compound 5 under the typical reaction conditions. Very interestingly, naphthalenes were significantly reduced while compounds 1–3 were increased. Importantly, the aromatics distribution in Fig. 3C' is quite similar to those of aromatics formed from PHB and CA (Fig. 1). We also noticed that the peaks of alkenes in Fig. 3C' were much higher than those in Fig. 1, which was attributed to the excessive 2-propanol used in the reaction. These results indicate that both compound 5 and propylene were the key intermediates for the formation of main alkyl benzenes (compounds 1–3). Compounds 2 and 3 might be formed *via* an acid-catalyzed Diels–Alder reaction¹³ from propylene and compound 5, followed by acid catalytic dehydration. Similar to the alkylation of toluene with propylene (Fig. S1†) in the typical reaction conditions, compound 2 could react with propylene through a 2-propyl carbocation mechanism to form compound 1, the major aromatic component of liquid oil (Scheme 4).

Compound 6, another unsaturated ketone, could also be converted into aromatics in the typical reaction conditions with or without propylene (Fig. 3D and E). In the presence of propylene, compound 6 was converted to several substituted benzenes (compounds h–j in Fig. 3E), which was also detected in the final hydrocarbon oil from CA and PHB.⁵ However, none of the main compounds 1–4 were formed from compound 6 even in the presence of propylene. This fact indicates that compound 6 is an intermediate, but not the key intermediate of the main aromatics (compound 1–4) from PHB.



Scheme 5 A proposed acylation reaction of compound 3 with CA for the formation of 1-indanone,3,3,4,5,7-pentamethyl-(compound 4).

Based on the information above, it can be concluded that both decarboxylation and ketonization of CA occurred under the typical reaction conditions, the former provided propylene and the latter provided compound 5. The decarboxylation and ketonization are competitive for CA and the competition is affected by the concentration of H_3PO_4 solution. As shown in Table 3, the acyclic alkenes from propylene oligomerization are the major products in the 85% H_3PO_4 solution, while the aromatics from compounds 5 and 6 *via* ketonization become the major ones in the 100% solution. This result indicates that high concentration of H_3PO_4 is beneficial to the ketonization while low concentration of H_3PO_4 to decarboxylation. The composition of hydrocarbon oil can therefore be controlled by simply controlling the acid concentration.

3.7 Oxygen-containing aromatics

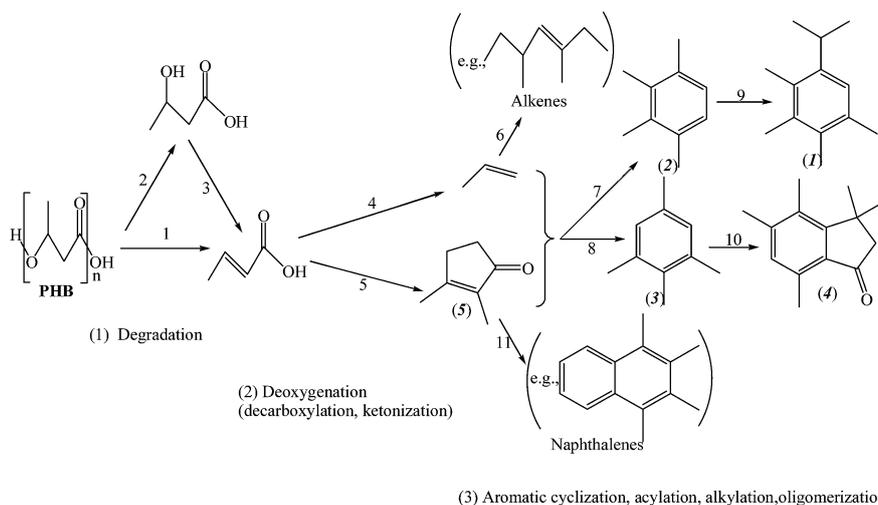
As shown in Fig. 1, compound 4 is an oxygen-containing aromatic compound in the hydrocarbon oil derived from PHB. It was not found in the controlled reactions of compound 5 or 6 with propylene (Fig. 3). Mostly likely, CA was involved in the formation of compound 4 *via* acylation of the aromatic compounds in the reaction conditions.¹⁴ In a controlled reaction of toluene and CA under the typical conditions, toluene was acylated with CA to form *H*-inden-1-one,2,3-dihydro-3,3-dimethyl-as a main product (Fig. S4†). It is therefore highly

possible that compound 3 was acylated with CA to form compound 4 as suggested in Scheme 5.

4 Summary

Based on the results above, the reaction routes from PHB to hydrocarbons are summarized in Scheme 6. The main sequential reactions can be divided into three stages: (1) degradation of PHB to monomeric compounds, (2) deoxygenation of crotonic acid, and (3) combination of the deoxygenated small molecules into final hydrocarbons.

In the first stage, H_3PO_4 is an effective catalyst in PHB hydrolysis and degradation (steps 1–3) and CA is the primary intermediate. Deoxygenation mainly occurred in the second stage, including decarboxylation and ketonization of CA to propylene and unsaturated ketones such as compound 5 (steps 4 and 5). The reactions are competitive for CA and are affected by H_3PO_4 concentration. In the third stage, multiple reactions occur including oligomerization of propylene (step 6), aromatic cyclization of propylene with compound 5 to form compounds 2 and 3 (steps 7 and 8), alkylation of propylene with compound 2 to form compound 1 (step 9), and acylation of compound 3 with CA to form compound 4 (step 10). In addition, deoxygenation of the O-containing ketones (compounds 5 and 6) leads to naphthalenes (step 11). In this overall reaction pathway, CA,



Scheme 6 Proposed reaction routes for the main compounds of hydrocarbon oil derived from PHB.

propylene and compound 5 are the key intermediates which determine the final composition of hydrocarbon oil.

Acknowledgements

The work is supported by Hawaii Natural Energy Institute and the Office of Naval Research.

Notes and references

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