

# PYROLYSIS OF BIOMASS MODEL COMPOUNDS USING FLASH VACUUM PYROLYSIS: MECHANISMS OF POLYCYCLIC AROMATIC HYDROCARBONS FORMATION

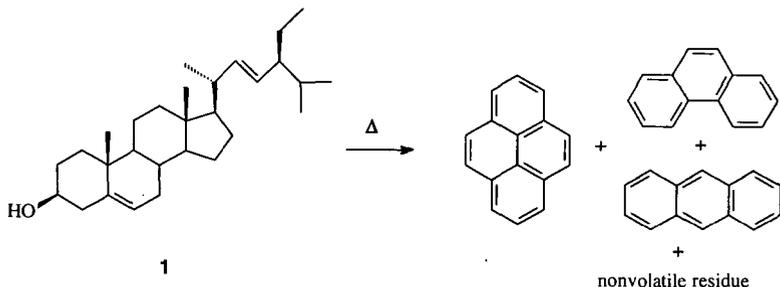
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**KEYWORDS:** Pyrolysis mechanisms, biomass model compounds, polycyclic aromatic hydrocarbons

## INTRODUCTION

There is a sharp contrast between the level of interest in the formation of polycyclic aromatic hydrocarbons (PAHs) and the level of understanding of their formation pathways. PAHs are classically formed from the incomplete combustion of carbon resources such as coal, petroleum, and biomass.<sup>1</sup> PAHs have also been found in emissions from incineration of plastic solid waste (polyethylene, polystyrene, polypropylene, and PVC),<sup>2</sup> emissions from home heating systems,<sup>3</sup> and in sites adjacent to high volume vehicle areas.<sup>4</sup> The formation of PAHs is of great interest in the thermal processing of carbonaceous materials, but there have been few detailed mechanistic studies on their formation pathways, and many of the mechanistic details, such as reaction intermediates and rate controlling step, are still largely unknown.

We are interested in the formation of PAHs in the thermal processing of coal and biomass into liquid products. Biomass model compounds such as plant sterols are known to yield PAHs under pyrolytic conditions. Badger et al. showed that atmospheric pyrolysis of stigmasterol (1)



at 700 °C yielded a complex mixture of hydrocarbons including pyrene, phenanthrene, and anthracene.<sup>5</sup> Although the authors speculated on possible mechanisms of PAH formation, there was no direct evidence for the proposed intermediates and reaction pathways. The pyrolysis of cholesterol has also been investigated in sealed tubes under conditions to simulate geochemical transformations (140 °C, 16 h).<sup>6a,b</sup> The degradation products included cholestane, cholestene isomers, and unidentified aromatic compounds; however, these studies were done on sediment support which may have induced acidic catalysis. Although there have been many studies on the formation of PAHs via thermal degradation of natural products, the reaction mechanisms and intermediates remain unclear.

The objective of this study is to gain fundamental insight into the reaction pathways that lead to PAHs in biomass model compounds. Flash vacuum pyrolysis (FVP) and atmospheric flow pyrolysis will be used as mechanistic probes for the identification of reaction intermediates and reaction pathways in the formation of PAHs. This investigation will focus on the pyrolytic degradation of plant sterols such as  $\beta$ -sitosterol (2a) and stigmasterol (1).

## EXPERIMENTAL

Benzene (EM) was freshly distilled from lithium aluminum hydride prior to use. Tetrahydrofuran (J.T. Baker, HPLC grade) was freshly distilled from potassium/benzophenone ketyl prior to use.  $\beta$ -Sitosterol (Acros, mixture of 79.6%  $\beta$ -sitosterol, 12.5% campersterol, and 7.6% stigmastanol by GC) was used without further purification. Gas chromatography was performed using a Hewlett-Packard 5890 Series II gas chromatograph equipped with a J&W Scientific 30 m  $\times$  0.25 mm id, 0.25  $\mu$ m film thickness DB-1 column and a flame ionization detector. Mass spectra were obtained at 70 eV on a Hewlett-Packard 5972 GC-MS equipped with a capillary column identical with that used for GC analysis. Relative molar responses were measured against *n*-tetradecane which was used as an internal standard.

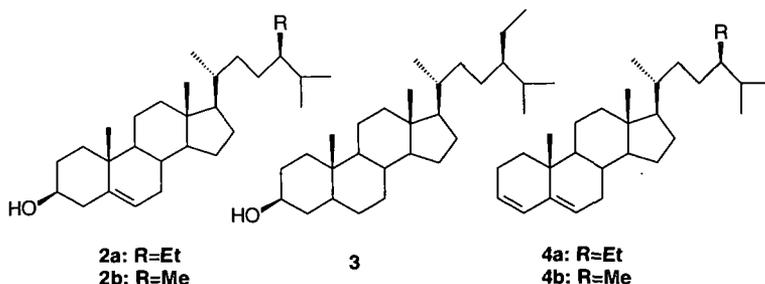
**FVP Conditions:** In a typical run, the substrate (typically 200 mg) was weighed into a pyrex sample chamber. The sample was warmed via an aluminum shroud wrapped with heat tape surrounding the sample chamber. The temperature of the shroud was monitored via a thermocouple. The sample chamber was attached to a 26 in. quartz tube (25 mm O.D.) via a 40/35 ground glass joint. The tube was packed with quartz chips (18 in.) to increase the residence time in the furnace. The other end of the quartz tube contained a right angle elbow with an O-ring joint (size 226) coupled to a Trahanovsky-style cold trap. The elbow was wrapped with heat tape and heated to ~65 °C to prevent deposition of the pyrolysate upon exiting the oven. The pyrolysis tube was heated by a horizontally mounted Carbolite tube furnace (model TZF 12/38/400) operating at a temperature range of 400 - 700 °C ( $\pm 2$  °C). The high vacuum end of the trap was equipped with an O-ring joint (size 226) that coupled to a vacuum connector. The sample chamber, quartz tube and trap were connected in series to an Edwards diffusion pump (model EO50/60) with a Welch DuoSeal mechanical backing pump (model 1405). High vacuum pressures ( $>10^{-3}$  Torr) were detected with a Hastings vacuum gauge; low vacuum pressures ( $<10^{-3}$  Torr) were detected with a Varian 571 Bayard-Alpert type hot filament ionization gauge head with a Varian Multi-Gauge display. FVP runs were typically performed at a baseline pressure range of  $2.0\text{-}7.0 \times 10^{-5}$  Torr.

**Preparation of *p*-Toluenesulfonic acid (3%)/Silica gel Dehydrating Reagent<sup>7</sup>:** A solution of *p*-toluenesulfonic acid monohydrate (2.96 g, 15.6 mmol) in acetone (20 mL) was added in one portion with rapid stirring to silica gel (99.96 g, Baker Analyzed, 60-200 mesh) in a 500 mL triple-neck round bottom flask equipped with an overhead mechanical stirrer. The mixture was stirred for 1 h at RT in an argon atmosphere. A vacuum adapter was attached to the flask and the volatiles were removed *in vacuo* (1.5 Torr) at 45-55°C with stirring. The TsOH/silica gel reagent was stored in a tightly stoppered round bottom flask prior to use.

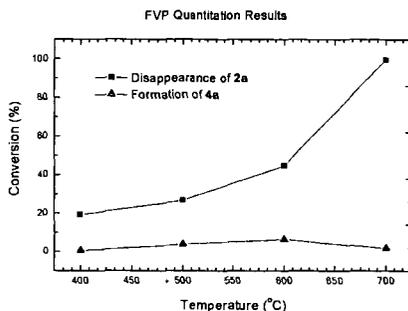
**Dehydration of  $\beta$ -Sitosterol:** A solution of  $\beta$ -sitosterol (0.83 g, 2.0 mmol) in dry benzene (170 mL) was added to 12.01 g TsOH/silica gel (3%) in a 500 mL round bottom flask equipped with a reflux condenser. The mixture was refluxed for 2 h in an argon atmosphere. The flask was allowed to cool to RT followed by addition of petroleum ether (100 mL, low boil). The contents of the flask were filtered through a 2 in. pad of silica gel and eluted with 1:1 benzene/petroleum ether (*v/v*). Solvent was removed from the filtrate *in vacuo* and the residue was flash chromatographed twice on silica gel using 100% hexane as the eluent. The yield of dehydration product **4a** was 0.33 g (0.84 mmol; 42% yield; 85% purity by GC); GCMS: *m/z* 396, ( $M^+$ , 100%).

## RESULTS AND DISCUSSION

The  $\beta$ -sitosterol was a mixture composed of three major compounds discernible by GC:  $\beta$ -sitosterol (**2a**), stigmastanol (**3**), and campesterol (**2b**) with effective (GC) molar ratios of 10.5, 1.7, and 1.0, respectively. We will focus on the pyrolysis pathways of **2a** since the pyrolysis of the methyl derivative **2b** should be very similar. The FVP of **2a** was investigated from



400 - 700 °C to determine the primary pyrolysis product in the degradation of sterols. The principal product observed by GC from the FVP of **2a** and **2b** is stigmasta-3,5-diene **4a** and **4b** respectively. Chemical confirmation was established through comparison of the GC retention times and MS data of the pyrolysate with an authentic sample of **4a** prepared by dehydration of **2a**. No other products (peaks) of any significance were observed by GC or GC-MS analysis. Figure 1 shows a plot of the percent conversion of **2a** and percent formation of dehydration product **4a** versus pyrolysis temperature. At lower FVP temperatures ( $< 500$  °C), the data show a trend that correlates the disappearance of **2a** with the appearance of **4a**. At higher



**Figure 1.** Conversion of **2a** and formation of **4a** as a function of temperature.

pyrolysis temperatures, a nonlinear increase in the disappearance of **2a** occur with concomitant decrease in the formation **4a**. This is an indication that at higher temperatures, either the dehydration products **4a** are undergoing secondary pyrolysis or a mechanism other than dehydration is operating. We are currently investigating the pyrolysis of dehydration product **4a** to determine if it forms PAHs. Preliminary results show that **4a** readily decomposes at 500 °C (36.2 % conversion) but few products are observed by GC analysis.

There is a significant discrepancy between the yield of **4a** (1-6 %) and the recovery of **2a** (see Figure 1). This discrepancy in mass balance may be due to fragmentation of the steroidal skeleton to form gaseous hydrocarbons. At high temperatures and low pressures,  $\beta$ -scission is faster than bimolecular hydrogen abstraction. Hydrocarbon radicals tend to break down all the way to a methyl radical or hydrogen atom and several molecules of ethylene (i.e. the Rice-Kossiakoff mechanism). We are investigating the formation of light gases from the FVP of **2a** by GC-MS and pyrolysis-GC-MS. We are also investigating the possibility that **2a** is undergoing a bimolecular condensation to form an ether which might not be volatile and would escape GC detection. We are currently screening the reaction mixtures by HPLC with refractive index detection.

Preliminary results have also been obtained on the atmospheric pyrolysis of **2a** at 500 °C. The major product by GC analysis is **4a**, i.e. dehydration. A significant number of products are formed in low yields. We are currently screening the reaction mixture by reverse-phase HPLC with diode array detection and GC-MS for PAHs.

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