Thermal cracking of triacylglycerols: Molecular beam studies

Ibrahim Alhroub, Wei Shen [1], Jin Yan, Mark Sulkes *

Chemistry Department, Tulane University, New Orleans, LA 70118, USA

ARTICLE INFO

ABSTRACT

Molecular beam methods have been employed to study the evolving product chemistry in the uncatalyzed low temperature (~280–380 °C) thermal cracking of triacylglycerols (TGs). The principal model TG studied was triolein, with additional experiments carried out on oleic acid and the model TG tristearin. A flow of He carrier gas entrained heated vapor from the samples, with sample temperatures gradually raised. The ensuing gas expansions were skimmed to form molecular beams. Soft ionization of neutral species in the beam was effected by laser pulses, followed by time of flight mass spectrometry. Depending on the frequency of the photoionization pulses, it was possible to monitor all or nearly all of the neutral pyrolysis species present or instead to monitor selectively only the aromatic species. Trends in the growth and diminution of product peaks could be understood and characterized better using multivariate analysis. In the model TGs considered, it was observed that thermolysis of the TG ester bonds was followed by additional chemistry involving the detached fatty acid fragments. The presence of a double bond in the fatty acid side chain was found to facilitate fragmentation pathways that were initially prevalent. For both triolein and tristearin, a similar evolution of aromatic products was observed. As evidenced by 266 nm photoionization mass spectra, that selectively show aromatic products, the initial aromatic products appeared to be mainly phenyl derivatives of high mass (>200 amu). These products could have derived from intramolecular cyclizations of detached fatty acid species that led to aromatic ring formation.

1. Introduction

Beyond the transesterification of triacylglycerols (TGs) leading to biodiesel fuels [1], pyrolysis of TGs is an approach that allows for the transformation of plant oils into renewable sources of transportation fuels, including gasoline, and other desirable organic products [2]. Fig. 1 shows the structure of triolein, a TG consisting of a glycerol backbone containing three ester linked oleic acid molecules. While TGs presently offer far less fuel production potential than lignocellulosic biomass feedstocks [3], there are several factors in their favor. First, pyrolysis of TGs can produce high yields of transportation fuel components (small alkanes and alkenes) with relatively little further refining, whereas the bio oil resulting from biomass pyrolysis is still far from yielding refined transportation fuel [3]. In addition, microalgaes, a non-edible renewable source of TGs, have extremely high lipid contents [4], affording TG production rates 45–220 times higher than terrestrial biomass [3]. As the

limiting factor of microalgae growth production cost is improved, TGs hold promise as a much more important renewable source of fuels and organic chemical products [1,4].

There has been continuing study of the pyrolysis chemistry of TGs [2,5–13], with and without catalysts, although the total volume of this work is less than studies of lignocellulosic biomass pyrolysis. In much of the research, TG cracking has been carried out in small reactors, with temperatures from the low 300 °C range to over 500 °C, with and without catalysts. Subsequent analysis has been carried out to identify and quantify terminal products, particularly using GC and also in some cases IR. Efforts have been made to account to the greatest extent possible for all products on a % (w/w) basis. Overall terminal product distributions found can vary significantly in composition. Nonetheless, some recent work indicates that it might be possible to produce a high percentage of low molecular weight organic liquid products via pyrolysis at relatively low temperatures (low 400 °C) without catalysts [10].

Guided by chromatographic analyses of final products by type and amount, important aspects of TG pyrolysis chemistry have been addressed by working to infer early chemical steps that strongly influenced observed product branching ratios [2,5–19]. Molecular beam based methods, not yet applied to TG pyrolysis, offer the possibility of direct observation of evolving product chemistry. Rare
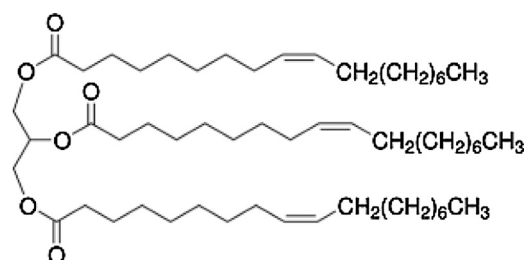
Fig. 1. Structure of triolein. The double bond in the fatty acid chains is replaced by a single bond for tristearin.

Fig. 2. Schematic of molecular beam experimental method.

gas entrained product supersonic gas expansions are complete in a matter of microseconds [20], internally cooling whatever reactive species were present just prior to the gas expansions. In the present work, we flowed He over continuously heated TG samples. A future goal is application of heating on shorter timescales prior to the gas expansions. The approach of applying fast impulses (photolysis, corona discharge, pyrolysis) to initial reactants has facilitated the production in molecular beams of many *discrete* species specifically targeted for study, usually reactive [21–30]. For TG pyrolysis, however, we instead wish to observe the *entire* set of species produced, or selected subsets. We previously used this approach to study product chemistry following corona discharges on alkylbenzenes [31,32]. A synchrotron based group also has reported similar electrical discharge product chemistry studies [33–36].

Central to our molecular beam approach is time of flight mass spectrometry (TOFMS) initiated by soft laser photoionization (PI). The recorded ion masses observed should generally correspond to the masses of the neutral parent species (i.e., parent ion fragmentation is not extensive). We employ PI methods that allow for mass detection of either nearly all neutral species present or, alternatively, selective mass identification of aromatic species only. However, only occasionally can parent ion mass values alone serve to identify species. Thus our present goal is to characterize generally the pathways observed for early pyrolysis chemistry products, well before reaching the terminal product distributions for pyrolysis in reactors [9,10].

Our approach has resemblances to the method of molecular beam mass spectrometry (MBMS), long employed to study lignocellulosic biomass pyrolysis [37,38]. In these experiments biomass is introduced into heated quartz tube pyrolyzers with rare carrier gas flow entraining the evolving products. At the pyrolysis tube exit the vapor flow is skimmed into a molecular beam in order to be introduced into a mass spectrometer, normally in this work electron impact ionization followed by a quadrupole mass spectrometer. As a function of flow time/temperature, changing overall product mass spectra are recorded. In MBMS, even with the relatively low electron impact potentials typically used (∼20 eV), a nontrivial amount of fragmentation likely occurs. In contrast, our implementation of 10.5 eV single photon ionization in TOFMS should result in ionization of almost all neutrals present but with less significant ion fragmentation. In addition, use of multiphoton ionization spectroscopies allows for ionization/detection of selected compound classes from among all the products [39,40].

Our experiments produce TOFMS that show product evolution in real time—sets of mass detected products that even in the latest observed stages may still vary significantly from the terminal product distributions analyzed in pyrolysis reactor experiments. To discern evolving trends more clearly, the profitable use of multivariate analysis dates from the 1980s, when it began to be applied to analysis of lignocellulosic biomass pyrolysis data [37,41–44]. Multivariate analysis facilitates clearer identification of correlated trends in the growth and diminution of various peaks detected in the mass spectra.
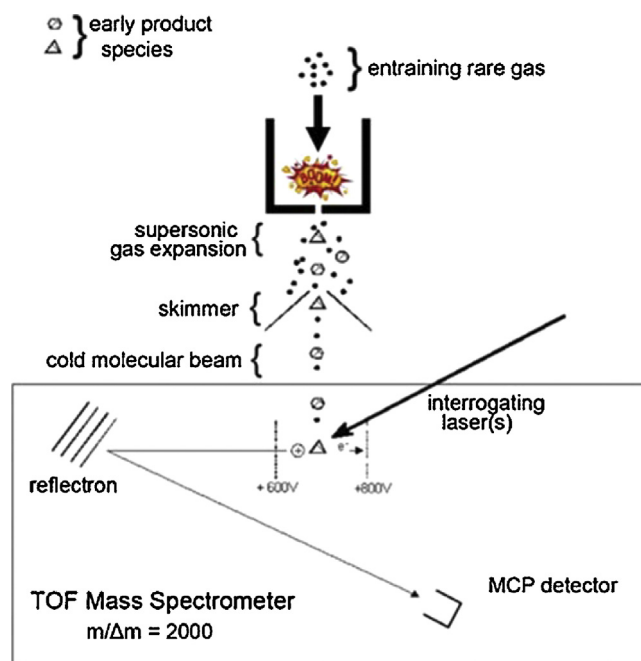
2. Experimental

An overall experimental schematic is shown in Fig. 2. He carrier gas was passed over heated samples to entrain volatile products; the seeded vapor then underwent supersonic expansion, cooling and stabilizing the entrained products present at that time. The center stream of the gas expansions was skimmed to produce molecular beams. Laser pulses effected soft photoionization of the products, followed by TOFMS.

2.1. TGs and related samples

Experiments were done primarily on triolein, a model TG consisting of a glycerol backbone with three ester linked oleic acid side chains (Fig. 1). The mass spectrometry in this case, with all the fatty acid side chains being identical, will be less complicated than would be the case with naturally occurring TG samples. In addition, the subcomponents of triolein, oleic acid and glycerol, were studied. Experiments were also carried out with another model TG, tristearin, containing three stearic acid side chains. Compounds with purity >99% were obtained from Sigma–Aldrich and used without further treatment.

2.2. Sample handling methods

We employed resistive heating methods, querying product chemistry as a function of sample temperature. Subsequently, we intend to attempt short timescale pyrolysis by heating sample substrate surfaces with laser pulses, but electrical heating was the most straightforward initial approach.

In principle, a pulsed gas expansion, as opposed to a continuous one, should be the best method of proceeding. The advantages of a pulsed gas expansion include: greatly reduced pumping requirements, allowing for high He backing pressures (e.g., 10 atm); resulting strong entraining gas pulses, producing supersonic expansions with optimal cooling; stronger product species signals, since orifice diameters can be made quite large (1 mm or more); significantly minimized retention time of volatilized products before entrainment and gas pulse expansion compared to a