Fuel xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

DFT study of the acid-catalyzed ethanolysis of butyric acid monoglyceride: Solvent effects

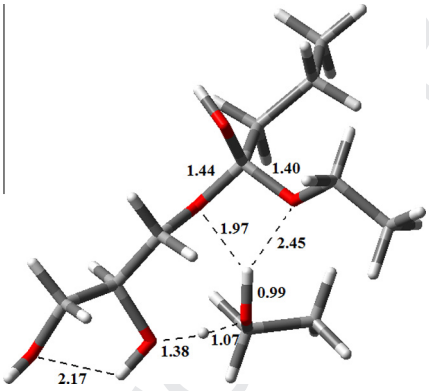
Augusto Cesar Huppes da Silva [a], Evandro L. Dall'Oglio [a,*], Paulo T. de Sousa Jr. [a], Sebastião Claudino da Silva [a], Carlos Alberto Kuhnen [b]

[a] Departamento de Química, Universidade Federal do Mato Grosso, Av. Fernando Corrêa da Costa s/n, Coxipó, Cuiabá MT CEP 78090-600, Brazil
[b] Departamento de Física, Universidade Federal do Santa Catarina, Campus Universitário, Trindade, Florianópolis SC CEP 88040-970, Brazil

HIGHLIGHTS

- DFT calculation with micro solvation shows the formation of an intermediate adduct.
- Tetrahedral adduct stabilized by assisted proton transfer by added solvent molecule.
- The structure of the intermediate is stabilized by the formation of two rings.
- The rate determining step is the decomposition of the intermediate adduct.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 July 2013
Received in revised form 6 November 2013
Accepted 10 November 2013
Available online xxxx

Keywords:
Acid catalysis
Transesterification
Micro-solvation
DFT calculations

ABSTRACT

The reaction mechanism of the acid-catalyzed transesterification of butyric acid monoglyceride was studied employing Density Functional Theory (DFT). Solvent effects were included by means of the integral equation formalism for the polarizable continuum model (IEFPCM). It was found that both in the gas phase and in solution the reaction proceeds through a concerted mechanism with a single transition state (TS) and without the formation of a tetrahedral intermediate. The inclusion of micro-solvation to model the transesterification reaction led to a stepwise mechanism where the rate determining step is the decomposition of the intermediate adduct and the formation of the tetrahedral intermediate has a lower energy barrier. The structure of the intermediate is stabilized by the formation of two rings making the glycerol backbone more rigid and contributing to stabilizing the tetrahedral intermediate by lowering the total energy of the system due to its intrinsic H bonds.

© 2013 Published by Elsevier Ltd.

1. Introduction

The environmental and economic issues raised by the rapid growth in the global population coupled with industrial and technological developments and the prospect of the depletion of limited fossil fuel resources are driving the search for new renewable sources of energy such as biodiesel. Biodiesel consists of fatty acid alkyl esters derived from renewable energy sources such as vegetable oils and animal fats. Biodiesel is biodegradable, non-toxic and hardly inflammable, and it has a good combustion-emission profile with less carbon monoxide and unburned hydrocarbons when compared to fossil fuels and no sulfur dioxide production [1]. The main process used to obtain this important source of energy is through transesterification reactions (alcoholysis of carboxylic esters under basic or acid conditions),

* Corresponding author. Tel./fax: +55 65 3615 8798x8799.
E-mail address: dalloglio.evandro@gmail.com (E.L. Dall'Oglio).

0016-2361/$ - see front matter © 2013 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.fuel.2013.11.023

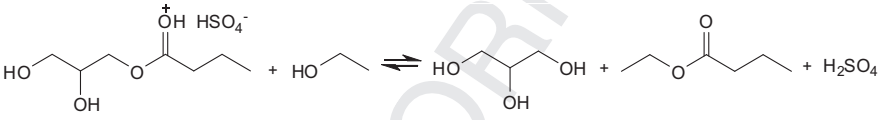
Please cite this article in press as: da Silva ACH et al. DFT study of the acid-catalyzed ethanolysis of butyric acid monoglyceride: Solvent effects. Fuel (2013), http://dx.doi.org/10.1016/j.fuel.2013.11.023

UNCORRECTED PROOF

which involve the reaction of alkyl alcohol with vegetable oils or animal fats to yield monoalkyl esters and glycerol. Following the early experimental studies by Freedman et al. [2] on the alkaline and acid-catalyzed transesterification of some vegetable oils, only a few reports on the kinetics of vegetable oil transesterification had been published by the end of the 1990s. However, in more recent years, increasing energetic needs have been the driving force behind renewed interest in biodiesel production, as evidenced by the vast number of publications on this subject in the past 10 years [3–7].

However, there are few theoretical approaches concerning the reaction mechanism involved in the transesterification of long-chain triglycerides for biodiesel production using a high level of theory. The alkaline-catalyzed transesterification of palmitic, oleic and linoleic acid monoacylglycerides was investigated earlier by means of AM1 calculations [8], and Hartree–Fock (HF) calculations using the STO-3G basis set were performed [9] to study the alkaline-catalyzed transesterification of homologous triacylglycerides, from C4 (butyric acid) to C18 (oleic and linoleic acid). More recently Density Functional Theory (DFT) calculations were employed to study the alkaline transesterification of the pentylic acid triglyceride [10] and of the butyric and pentylic acid monoglycerides [11,12] in the gas phase, including solvent effects. Concerning acid catalysis, DFT calculations were recently reported [13] for the methanolysis and hydrolysis of glycerol triacetate as a model compound of a triacylglycerol and a DFT study on the gas phase acid-catalyzed ethanolysis of butyric acid triglyceride was carried out [14]. These DFT calculations [13,14] indicate that transesterification occurs by preferentially attacking the ethanol at the center ester bond of the triacylgycerol backbone, which is in good agreement with recent NMR measurements performed by Jin et al. [15] in relation to the methanolysis of vegetable oil.

In the present study the DFT calculations were performed for the gas-phase, in solution and in solution with micro-solvation. Due to the high number of electrons in such calculations with triglycerides and diglycerides, instead of considering the three steps involved in the transesterification process, for simplification, we investigated the reaction mechanism of the third step in the transesterification of triacylglyceride, that is, the specific reaction given in Eq. (1).



(1)

Ethanolysis of protonated monoacylglycerol.

2. Calculation methods

The acid-catalyzed reaction was studied in the gas phase and in solution by optimizing the geometries and energies of all species employing Density Functional Theory (DFT) using Becke's three-parameter hybrid exchange functional, the Lee–Yang–Parr correlation functional (B3LYP) and the 6–31G(2d,p) basis set. In order to better describe the reaction energy, MP2 single point calculations were performed to improve the energy evaluation. Vibrational frequency calculations were carried out on all of the optimized structures to confirm all of the first-order saddle points and local minima on the potential energy surfaces. Transition states were also confirmed by viewing the motion of the imaginary vibrational mode. Intrinsic reaction coordinate (IRC) calculations were performed to verify the expected connections between the first-order saddle point and local minima on the potential energy surfaces.

The solvent effects were included by using the integral equation formalism for the polarizable continuum model (IEFPCM) [16] implemented in the Gaussian package [17]. To simulate the reaction in solution ethanol was used as the solvent with a dielectric constant of 24.85. In solution, taking into account the explicit presence of one molecule of solvent (ethanol) acting as a micro-solvent, diffuse functions were employed using the 6–31+G(d,p) basis set in IEFPCM calculations.

3. Results and discussion

Regarding the transesterification stepwise reaction mechanism, for acid-catalyzed reactions in the gas phase and in solution (without micro-solvent), many unsuccessful attempts were made to obtain the structures of the transition states and intermediaries. DFT calculations in the gas phase and DFT/IEFPCM calculations in solution showed that the reaction proceeds through a concerted mechanism. The free energies of activation and of the reaction obtained with the DFT/B3LYP/6–31G(2d,p) calculations are shown in Table 1. Correlation effects were accounted for with an MP2 single point calculation in both the gas phase and in solution. Table 1 also shows the results with ethanol as a continuum medium and the explicit presence of one ethanol molecule as a micro-solvent.

As shown in Table 1, in the gas phase and in solution (without micro-solvation) DFT calculations indicate one transition state with a concerted mechanism. The concerted reaction involves two (or more) bond formation or breaking processes which occur concomitantly as the reaction proceeds. Therefore, there is no discrete or discernible intermediate with a finite lifetime along the reaction pathway. The question of whether or not ester alcoholysis can be concerted has been addressed by a number of groups and experimental support for a concerted mechanism of acyl transfer has been evidenced [18]. Williams [19] developed a theory to predict when ester alcoholysis will be concerted and when it will proceed through stepwise reactions via a tetrahedral intermediate. Based on ion cyclotron resonance (ICR) experiments, Kim and Caserio [20] showed the concertedness of acyl group transfer in gas-phase reactions and ICR techniques applied by Takashima et al. [21] to the hydrolysis of esters showed a slow isotopic oxygen exchange in the gas phase, while their thermochemical estimates suggested that the tetrahedral adduct was more likely to be a local transition state rather than a stable intermediate. Fox et al. [22] performed a theoretical *ab initio* study addressing the question of whether nucleophilic addition to the carbonyl groups of acid chlorides, esters and anhydrides involves an addition–elimination pathway or proceeds via a concerted S_N2-like mechanism in the absence of a tetrahedral intermediate. Their results corroborate earlier suggestions that the methanolysis of acetyl chloride and of protonated methyl acetate does not occur through the generally accepted addition–elimination pathway. In contrast, the gas phase calculations for the neutral hydrolysis of ethyl acetate [23] showed the existence of an S_N2-like mechanism with activation energies around 10 kcal mol^{-1} higher than those of the addition–elimination pathway.

UNCORRECTED PROOF

Please cite this article in press as: da Silva ACH et al. DFT study of the acid-catalyzed ethanolysis of butyric acid monoglyceride: Solvent effects. Fuel (2013), http://dx.doi.org/10.1016/j.fuel.2013.11.023

Download English Version:

https://daneshyari.com/en/article/6638107

Download Persian Version:

https://daneshyari.com/article/6638107

Daneshyari.com