Chemistry and Physics of Lipids 163 (2010) 172–181

Contents lists available at ScienceDirect

Chemistry and Physics of Lipids

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

Determination of enthalpy of formation of methyl and ethyl esters of fatty acids

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ARTICLE INFO

Article history:
Received 1 July 2009
Received in revised form 6 October 2009
Accepted 5 November 2009
Available online 14 November 2009

Keywords:
Esters
Enthalpy of formation
Heating value
Gaussian
Estimation methods

ABSTRACT

Biofuels composed by fatty acid methyl esters are widely used as partly substituting fuels for diesel fossil fuels. Additionally, it is expected that the diesel biofuel norms will be extended to ethyl esters produced from bioethanol in the upcoming years. A precise knowledge of the standard enthalpy of formation is necessary for the calculation of some parameters useful for the analysis of the combustion process and emissions of a diesel engine operating with different fuels, such as the heating value, the adiabatic flame temperature or the kinetic mechanisms. However, experimental data for this property are scarce, and only available for short-chain, saturated methyl esters. In this work, four estimation methods for the calculation of the enthalpy of formation are examined and compared. Three of them are simple methods based on groups or bonds contribution, and another one is a computational method (with Gaussian 03 software). After presenting the implementation rules for each of them, conclusions are stated based on the results attained. Gaussian and Benson-Groups methods seem to be more accurate in predicting the actual values of the enthalpy of formation, both methods considering the separation between double bonds and the edge effects in the molecule. However, only the Gaussian method considers the effect of the position of the double bond in the molecule for all the unsaturated esters.

1. Introduction

Fatty acid esters of vegetable oils or animal fats are nowadays the main components of diesel biofuels, and it is expected that this situation will remain for the next decades, since many of the future technologies for the production of diesel-like fuel alternatives will still transform differently obtained organic oils into esters (Chisti, 2007; Galán et al., 2009; Fabbri et al., 2007; Modi et al., 2007). Although the traditional transesterification process of the oil is usually made with fossil-derived methanol, the use of bioethanol provides an additional renewable potential to the produced fuel and, in general, a decrease in the life-cycle greenhouse emissions, whose limitation will soon entry into force in Europe (European Parliament, 2008). Nevertheless, quality standards (EN-14214, 2008) are only established, up to now, for fatty acid methyl esters, which must constitute more that 96.5% in mass of the total fuel. In addition, the unsaturation is limited in various ways, i.e. through the iodine number, through the mass content of linolenic acid methyl ester (limited to 12%) and through the total poly-unsaturated esters (limited to 1%).

Although these restrictions are expected to provide a protection for some properties (i.e. oxidation stability and cetane number), they also prevent from using many natural oils as a feedstock for biodiesel production (Knothe, 2002). The extension of the range of oil sources to other wastes or non-edible seeds (for example, lineseed, waste fish or microalgae oils) would permit the use of autochthonous or massive feedstock which would contribute to improve the economic, energy and sustainability balances of liquid biofuels. Moreover, the possibility of designing the composition of the oil to be used for targeted biodiesel production (not only for automotive uses but also for aircrafts with even more restrictive requirements) either by blending different feedstock or by genetic modifications of oilseed plants (Kinney and Clemente, 2005) would open the range of biodiesel compositions and properties and would make the economic and environmental objectives compatible with the quality specifications of the fuels.

The mentioned perspective of oil composition selection, together with the expected variety in the composition of oils will make necessary in the future the estimation of the thermochemical properties of the biodiesel fuels as a function of their fatty acid esters profile. The database of basic esters to be used in the estimation tools analysed in this paper has been extended to all the usual esters found in vegetable- or animal-derived oils, including those esters with carbon chains shorter than usual, in order to confirm their experimental agreement.

A good estimation of the enthalpy of formation is the basis for the calculation of some essential parameters associated with the engine performance and emissions, such as the heating value, the adiabatic flame temperature and the detailed combustion kinetics (Blanquart and Pitsch, 2007).

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doi:10.1016/j.chemphyslip.2009.11.002

2. Calculation methods

The gas-phase standard enthalpy of formation was estimated by two different group contribution methods. These methods proceed by dividing the chemical molecule of the evaluated compound into a list of simple functional groups, each of them having a specified numerical contribution to the thermochemical property that is to be estimated. Thus, the simplicity is the main advantage of these methods since only the structure of the molecule is needed to perform the calculation. Although good agreement can be achieved between these estimations and the experimental data, the accuracy depends on the type of method and the complexity of the molecule.

The Joback method (Joback and Reid, 1987; Poling et al., 2000), an extension of the Lydersen method, is one of the most traditional contribution methods. The values assigned for each functional group are presented in Table 2. This method was applied (Poling et al., 2000) in order to estimate the standard enthalpy of formation of more than 300 compounds, reporting a mean deviation around 10% between them and the available experimental data. The Benson method (Poling et al., 2000; Cohen and Benson, 1993) is a more complicated (and more accurate) method, which considers not only the contribution of each functional group but also the interaction of one group with its neighbours (Table 4). In a reported work (Poling et al., 2000), the authors compared several methods over a wide set of representative compounds, and concluded that the Benson method provided the best estimations.

A simpler, but less precise, method for estimating thermochemical properties was also proposed by Benson (Benson and Buss, 1958). It is defined as a bond contribution method, thus the type of bonds are first identified and counted and then the value of the molecular property is calculated by adding the contribution of all bonds (Table 3).

In order to validate results for the standard enthalpy of formation obtained with the aforementioned methods, a widely acknowledged (Osmont et al., 2007; Baboul et al., 1999; Becke, 1988, 1992a,b, 1993a,b; Lee et al., 1988; Scott and Random, 1996) computational technique, Gaussian-3, was applied as well. Gaussian-3 (hereinafter G3) is a procedure used for molecular (fundamental vibrational frequencies, zero-point energy) and thermochemical (entropy and enthalpy) calculations, developed from the former version Gaussian-2. The improvements addressed in the most updated version, which are discussed in other sources (Fast et al., 1999), decrease the overall computational cost and the average error.

Gaussian-3 calculations are based on ab initio molecular orbital theory (Baboul et al., 1999), where principles of the statistical thermodynamics and quantum chemistry are applied. In its original structure, G3 executed the following summarized sequence over a previously specified basis set:

1. Optimization of the molecule geometry, by using the second order perturbation theory of Mollet–Plesset (MP2).
2. Calculation of the zero-point energies (ZPE), from Hartree–Fock theory (HF).
3. Calculation of various single-point energies at different levels of theory.

However, some deficiencies have been pointed out regarding this original method. Hartree–Fock theory is reported to overestimate the vibrational frequencies (Scott and Random, 1996), and although it can be partially compensated by introducing scale factors, these are not trivial and authors do not agree in which values to choose (Osmont et al., 2007). Besides, for the case of thermochemical calculation, such scale factors strongly depend on the thermochemical property that is to be calculated. Other related issue is whether the scale factors depend on the type of molecules analyzed or not.

Table 1
Atomic corrections.

Atom	c_i^* (hartree/atom)
H	0.581896
C	38.115345
O	75.150410

Other methods available to substitute the HF or MP theories are the semiempirical methods, such as AM1 and PM3, but few works have been published examining their use (Healy and Holder, 1993; Peterson et al., 1995), and their advantages and drawbacks are not well understood.

A simple variation of the original G3 method that performs well was initially introduced by Bauschlicher and Partridge (1995). It consists in applying a density-functional theory (DFT) during the first two steps of the above sequence, instead of the MP2 and HF theories. DFT includes an electron correlation when computing the vibrational frequencies (Scott and Random, 1996). This is believed to provide better results for larger systems (Baboul et al., 1999; Scott and Random, 1996), such as the esters molecules analyzed in the present work. The most popular of these theories is the B3LYP (Becke, three-parameter, Lee–Yang–Parr) exchange-correlation functional, whose benefits have been proved for long (Becke, 1988, 1992a,b, 1993a,b; Lee et al., 1988). For instance, Bauschlicher (1995) tested 53 molecules and reported better agreement with the experimental data when the B3LYP theory was applied instead of others. In a more extensive work, Scott and Random (1996) examined and compared different theories for 122 molecules. The B3LYP procedure (and other B3-based procedures) provided the best results at predicting the zero-point vibrational energies, enthalpy and entropy. Based on this, the authors concluded that the B3-based DFT theories are a cost-effective procedure in the determination of thermochemical quantities.

For the calculation of the gas-phase standard enthalpy of formation applying the G3 theory, a commercial software named "Gaussian 03" (Frisch et al., 2004) in addition to the equation proposed by Osmont et al. (2007), Eq. (1), have been jointly used in the present work. They validated that model and found that the deviation between the calculated and the experimental enthalpies of several carboxylic acids and their derived esters was 1.8 kcal/mol in average.

$$\Delta h_f^0 = 627.51\left(E + \mathrm{ZPE} + \mathrm{CT} + \sum_i \alpha_i c_i^*\right) \qquad (1)$$

where E (electronic energy), ZPE (zero-point energy) and CT (thermal correction), are the direct output of the software Gaussian 03, while α_i and c_i^* are, respectively, the number of atoms i in the considered molecule and the atomic correction for atom i. The atomic corrections proposed by Osmont et al. (2007) are shown in Table 1.

3. Implementation of contribution methods

For programming purposes, implementation rules applied to fatty acid esters have been developed for Joback group contribution method, Benson Bonds contribution method and Benson-Groups contribution method. The list of groups or bonds used (abbreviated as J_i, B_i or G_i, respectively) and their contributions to the total standard enthalpy of formation, as reported by Poling et al. (2000) (J_i contributions), Benson and Buss (1958) (B_i contributions) and Benson (1976), Cohen and Benson (1993) (G_i contributions, with slight differences between the data provided in both references) are listed in Tables 2, 3 and 4, respectively.