Analysis of thermochemical data of fatty acids and acetates on their base

V V Ovchinnikov, A A Kulakov, S A Maltseva
Kazan National Research Technical University named after A.N. Tupolev KNITU-KAI, K. Marx str. 10, Kazan, 420111, Russia
E-mail: chem_vvo@mail.ru

Abstract. The heat of vaporization, combustion, formation, entropy in different phases and the heat of capacity of fatty carbonic acids and their acetates were analyzed and was determined that all functions of these types of compounds depend from the number of valence electrons \( N \) from which is excluded the sum of lone electron pairs \( g \) as represented in equations

\[
\Delta_{vap,f,c}H^\circ = i \pm f(N - g)
\]

and

\[
S^\circ(C_p) = i \pm f(N - g)
\]

The coefficients \( f \) in the first equations is in the range \( 10^8-10^9 \) kJ·mol\(^{-1}\) electron\(^{-1}\), that corresponds to the same values \( f \) in the equations, which are related to combustion processes. Other coefficient \( i \) is different for each type of compounds. The received new seven equations can be used for the calculation of the same thermodynamic functions for other organic and especially bioorganic substances with fatty radicals.

1. Introduction

It is known during a long time that fatty organic acids is a very important and used class of the carbon derivatives in industry, agriculture and pharmaceutical industries and medical products [1]. In this connection it is possible to recollect such names of medical preparations as miristic, palmitinic, margarinic, steaerin and arachitic acids [1, 2]. This class of compounds is a subject of an intensive research of the scientists in the different fields: the study of synthesis, reaction, thermodynamics and others directions in our time also.

However, not only thermochemical properties of fatty carbonic acids of different structure are important for the technical needs and theoretical studies. Acetates and esters of fatty acids represent a large significance also. On this reason the analysis and mathematical treatment of all thermodynamic functions of these classes of derivatives of fatty acids are summed and considered in this paper.

It is known, that all mentioned above class of compounds exist in condensed phase. Taking this circumstance into account, we believed that consideration of their thermochemical properties should begin first of all from the heat of vaporization \( (\Delta_{vap}H^\circ) \). This parameter can be obtained at the use of Clausius-Clapeyron experimental approach (equation 1) [3]

\[
\ln \frac{P_2}{P_1} = \frac{-\Delta_{vap}H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

(1)

In equation (1) \( P_1 \) and \( P_2 \) are a pressures (in Pa or mm.Hg), \( R \) is an universal gaseous constant 8.314 J·mol\(^{-1}\)K\(^{-1}\), \( T_1 \) and \( T_2 \) are temperatures (in K) of the experiments.
The analysis of other thermodynamic functions of different organic compounds can be made by any ways also. In our previous work [4] it has been shown that all thermodynamic functions $\Delta_{\text{vap,c,f}}\Psi^\circ$ ($\Psi^\circ$ is the heat ($\Delta H^\circ$) of vaporization, combustion, formation and entropy ($S^\circ$) and heat capacity ($C_p$) of investigated organic molecules are connected with a parameter $(N - g)$ in the range of one-factor correlation analysis (eq. 2), where $N$ is a general number of valence electrons, $g$ is a number of lone electron pairs (two electrons) in molecules with heteroatoms

$$\Delta_{\text{vap,c,f}}\Psi^\circ = i \pm f(N - g).$$

(2)

The parameter $g$ is equal 2 for three-valence nitrogen and phosphorus atoms and similar elements of the group, $g$ is 4 for oxygen, sulfur etc., $g$ is zero for five-valence nitrogen and phosphorus etc., $g$ is 6 for halogens. The parameters $i$ and $f$ are stoichiometric coefficients. In this paper we represent the thermodynamic data of different fatty acids and their acetates.

2. Fatty acids

Fatty acids are an interesting and important type of acids because they make up a main chain of the structure of lipides. Such acids have usually an even number of carbon atoms and form an unbranched chain. Many fatty acids have one or several double bonds; they are titled as unsaturated fatty acids. Such type of acids plays an important role in biochemistry of the living organisms and in industry also.

The analysis of thermodynamic functions of dodecanoic (1), miristic (2), palmitic (3), margarinic (4), stearic (5) and arachidic acids (6) [5–11] (table 1) gave the similar equations (3–6, which have been received by the known method of the solution of simole equation like $Y = i + fX$ where $r$ is the correlation coefficient, $S_o$ is standard deviation, $n$ is the number of research compounds. The errors of $i$ and $f$ coefficient were received from the same method.

$$\Delta_{\text{vap}}H^\circ = (27.1 \pm 17.9) + (1.4 \pm 0.2)(N - g),$$

(3)

$r = 0.974$, $S_o = 7.3$, $n = 6$ (compounds 1–6).

$$\Delta_cH^\circ = (5.7 \pm 80.5) - (108.7 \pm 0.8)(N - g),$$

(4)

$r = 0.999$, $S_o = 32.0$, $n = 6$ (compounds 1–6).

$$\Delta_fH^\circ = (-433.5 \pm 50.1) - (4.9 \pm 0.5)(N - g),$$

(5)

$r = 0.977$, $S_o = 20.4$, $n = 6$ (compounds 1–6).

$$C_p = (201.7 \pm 17.7) + (2.9 \pm 0.2)(N - g),$$

(6)

$r = 0.992$, $S_o = 7.2$, $n = 6$ (compounds 1–6).

As can be seen, the correlation parameter $f$ is equal $-108.7$ (kJ·mol$^{-1}$) in the equation (4) for fatty acids and practically equal to the same for linear carbon acids with $C_1$–$C_{12}$ carbon atoms in radicals [12]

3. Acetates with radicals of fatty acids

The analysis thermodynamic properties of the big class of esters is useful for beginning with various functions of acetates, which have an important significance in theory of organic compounds and in different regions of industry [1,2]. The approach to this aim is the same, which was used in previous part: the creation of the definite number of equations, which reflect the interrelation of thermodynamic functions with the number of valence electrons of the examined molecules [12].
Table 1. Thermodynamic properties (kJ·mol⁻¹ and J·mol⁻¹·K⁻¹) of condensed fatty acids a.

| No | Compound, formula, \((N - g)\) | \(\Delta_{vap}H^\circ\) | \(-\Delta_cH^\circ\) | \(-\Delta_fH^\circ\) | \(S^\circ\) | \(C_p\) |
|----|--------------------------------|---------------------|---------------------|---------------------|-------------|---------|
| 1  | Dodecanoic acid, \(\text{C}_{12}\text{H}_{24}\text{O}_2, 68\) | 127.9 | 7377.0 ± 0.9 | 775.1 | 404.3 |
| 2  | Miristic acid, \(\text{C}_{14}\text{H}_{28}\text{O}_2, 80\) | 139.7 ± 3.8 | 8676.7 ± 1.4 | 834.1 ± 4.2 | 432.0 |
| 3  | Palmitic acid, \(\text{C}_{16}\text{H}_{32}\text{O}_2, 92\) | 154.4 ± 4.2 | 10028.6 ± 1.9 | 848.4 ± 2.2 | 452.3 | 463.4 |
| 4  | Margarinic acid, \(\text{C}_{17}\text{H}_{34}\text{O}_2, 98\) | | 10624.4 ± 1.7 | 924.4 | 475.7 |
| 5  | Stearic acid, \(\text{C}_{18}\text{H}_{36}\text{O}_2, 104\) | 166.5 ± 4.2 | 11336.8 ± 2.1 | 947.2 ± 2.2 | 435.6 | 501.5 |
| 6  | Arachidic acid, \(\text{C}_{20}\text{H}_{40}\text{O}_2, 116\) | 199.6 ± 7.5 | 12574.2 ± 1.5 | 1012.6 ± 5.1 | 545.1 |

Fatty acids

| No | Compound, formula, \((N - g)\) | \(\Delta_{vap}H^\circ\) | \(-\Delta_cH^\circ\) | \(-\Delta_fH^\circ\) | \(S^\circ\) | \(C_p\) |
|----|--------------------------------|---------------------|---------------------|---------------------|-------------|---------|
| 7  | Methyl dodecanoate, \(\text{C}_{13}\text{H}_{26}\text{O}_2, 74\) | 70.7 ± 0.2 | 8117.0 ± 0.4 | 714.6 | |
| 8  | Methyl hexadecanoate, \(\text{C}_{17}\text{H}_{34}\text{O}_2, 98\) | 96.8 ± 0.6 | 10669.0 ± 0.4 | 879.5 | 495.1 | 474.5 |
| 9  | Methyl palmitoleate, \(\text{C}_{17}\text{H}_{32}\text{O}_2, 96\) | 96.4 ± 0.7 | 10547.0 ± 1.5 | 715.1 | |
| 10 | Methyl octadecanoate, \(\text{C}_{19}\text{H}_{38}\text{O}_2, 110\) | 105.9 ± 1.4 | 11962.0 ± 0.4 | 945.6 | |
| 11 | Methyl elaidate, \(\text{C}_{19}\text{H}_{36}\text{O}_2, 108\) | 77.2 | 11885.0 ± 12.0 | 731.7 | |
| 12 | Methyl linoleate, \(\text{C}_{18}\text{H}_{34}\text{O}_2, 106\) | | 11690.1 ± 1.5 | 645.7 | |
| 13 | Methyl linolenate, \(\text{C}_{18}\text{H}_{32}\text{O}_2, 104\) | 110.5 ± 0.5 | 11506.0 ± 1.5 | 544.0 | |
| 14 | Methyl oleate, \(\text{C}_{19}\text{H}_{36}\text{O}_2, 108\) | 104.0b ± 6.0 | 11832.4 ± 1.5 | 727.6 | |
| 15 | Methyl eicosanoate, \(\text{C}_{21}\text{H}_{42}\text{O}_2, 122\) | 116.4 ± 1.5 | 13263.0 ± 0.4 | 1003.0 | |
| 16 | Methyl ester of cis-11-eicosanoic acid, \(\text{C}_{21}\text{H}_{40}\text{O}_2, 120\) | 115.8 ± 0.7 | 13190.0 ± 0.3 | 791.0 | |
| 17 | Butyl ester of oleic acid, \(\text{C}_{22}\text{H}_{42}\text{O}_2, 126\) | 97.7 | 13843.0 ± 14.0 | 816.9 | |

Acetates with fatty radicals

| No | Compound, formula, \((N - g)\) | \(\Delta_{vap}H^\circ\) | \(-\Delta_cH^\circ\) | \(-\Delta_fH^\circ\) | \(S^\circ\) | \(C_p\) |
|----|--------------------------------|---------------------|---------------------|---------------------|-------------|---------|
| 18 | Methyl ester of cis-11-eicosanoic acid, \(\text{C}_{21}\text{H}_{40}\text{O}_2, 120\) | 115.8 ± 0.7 | 13190.0 ± 0.3 | 791.0 | |

a All thermodynamic data were compiled from [13].
b Average of 6 values.
The dependences of the heats of vaporization, combustion, formation and heat of capacity of acetates of fatty acids (7–17, table 1) and their interrelations with parameter \((N - g)\), as shown in the previous part, are reflected in the equations (7–9).

\[
\Delta_{\text{vap}}H^\circ = (4.8 \pm 10.6) + (0.9 \pm 0.1)(N - g),
\]

\(r = 0.967, S_o = 4.1, n = 10\) (compounds 7–11, 13–17).

\[
\Delta_r H^\circ = (-54.7 \pm 171.7) - (109.1 \pm 1.6)(N - g),
\]

\(r = 0.999, S_o = 72.6, n = 11\) (compounds 7–17).

\[
\Delta_f H^\circ = (-201.3 \pm 205.5) - (6.5 \pm 2.0)(N - g),
\]

\(r = 0.880, S_o = 72.6, n = 4\) (compounds 7–9, 15).

**Conclusion**

Thermodynamic parameters (heat of vaporization, combustion, formation in different phases, entropy and the heat of capacity) of 17 derivatives of fatty carbonic acids and their acetates were analyzed for the first time and was determined that all functions depend from the number of valence electrons \(N\) from which is excluded the sum of lone electron pairs \(g\) as represented in 7 equations \(\Delta_{\text{vap,c,f}} H^\circ = i \pm f(N - g)\) and \(S^o(C_p) = i \pm f(N - g)\). Necessary to note, that the stoechiometric coefficient \(f\) in equations (4) and (8) is in the range \(10^8\)–\(10^9\) kJ·mol\(^{-1}\) electron\(^{-1}\) in the received dependences, that corresponds to the same values \(f\) in the works, which are mentioned earlier for linear organic acids. Other coefficient \(i\) differs for each type of compounds and not necessity in the discussion. We compared the literary magnitude of the heat of combustion of 13-docosenoic fatty acid (\(\Delta_r H^\circ = -42802.3\) kJ·mol\(^{-1}\)) [14], with the calculated on the equation (4) (\(\Delta_r H^\circ = -42604.7\) kJ·mol\(^{-1}\)) and received the error in 4.6%.

This fact can serve as a proof of our right approach to the analysis of thermochemical data of fatty acids and their acetates.

**References**

[1] Jones M and Fleming S A 2010 *Organic Chemistry* (4th W.W. Norton & Company, Inc.)
[2] Bloch D 2007 *Organic Chemistry Demystified* (McGraw-Hill)
[3] Cox J D and Pilcher G 1970 *Thermochemistry of Organic and Organometallic Compounds* (New York: Academic Press)
[4] Ovchinnikov V V 2017 *Curr. Phys. Chem.* 7 313–336
[5] Lebedeva N D 1964 *Russ. J. Phys. Chem. (Engl. Transl.)* 38 1435–1437
[6] Schaake R C F, van Miltenburg J C and De Kruif C G 1982 *J. Chem. Thermodynam.* 14 771–778
[7] Adriaanse N, Dekker H and Coops J 1965 *Rec. Trav. Chim. Pays/Bas.* 84 393–407
[8] Wirth H, Droege J and Wood J 1956 *J. Phys. Chem.* 60 917–919
[9] Davies M and Malpass V E 1961 *J. Chem. Soc.* 1048–1050
[10] Singleton W S, Ward T L and Dollear F G 1950 *J. Am. Oil Chem. Soc.* 27 143–146
[11] Stephenson R M and Malanowski S 1987 *Handbook of the Thermodynamics of Organic Compounds* DOI:10.1007/978-94-009-3173-2
[12] Ovchinnikov V V 2014 *Bull. Kazan Technol. Univ.* 17 144–146
[13] National Institute of Standard Technology (NIST) of USA, Chemistry WebBook, URL http://webbook.nist.gov/chemistry.html
[14] Freedman B, Bagby M and Khory H 1989 *J.Am.Oil.Chem.Soc.*) 66 595–596