Thermodynamic Characteristics of Ethyl-2-cyano-3-(furan-2-yl)-prop-2-enoate Derivatives

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Abstract. Using bomb calorimetry and Knudsen effusion methods the enthalpic characteristics in condensed state of ethyl-2-cyano-3-(furan-2-yl) prop-2-enoate derivatives were experimentally determined. The values of the enthalpies of formation in the gas state of investigated esters were calculated taking into account the values of the enthalpies of sublimation adjusted to 298K. From obtained thermochemical values we defined new group contributions which can be added to the Benson’s additive scheme. Using these increments the enthalpies of formation of investigated compounds in gas state were theoretically calculated and their differences from the experimentally determined were analyzed.

Keywords: Bomb calorimetry, effusion method, Benson’s scheme

1 Introduction

Heterocyclic compounds are widely distributed in nature [1]. Many of them are particularly important for living organisms and they serve as a key components of biological processes. Many of drugs are derived from natural products, but their number is much greater than those synthesized from natural or synthetic compounds [2]. In particular, furan derivatives are commonly used in the synthesis of biologically active compounds that exhibit antibacterial, antitumor, and tuberculostatic action [3]. Determination of thermodynamic properties of substances with widespread use will help to optimize the processes of their synthesis and processing, as well as providing an opportunity to explore the energetic properties of molecules of this class. Considering these diverse information the need of a greater number of values of thermochemical parameters for esters of furanacrylic acid becomes evident. Despite this there are no reported in literature values of the standard molar enthalpies of formation in the crystalline and gas phase, as well as the standard molar enthalpies of sublimation of investigated compounds.

The present study provides results of the purification, standard molar energy of combustion, standard molar enthalpy of sublimation, and standard molar enthalpy of formation in both crystalline and gaseous states, T = 298.15 K, for the five compounds. The experimental determination of the standard energies of combustion of the five esters in oxygen at T = 298.15 K was conducted using static-bomb combustion calorimetry. From the temperature dependence of the vapour pressure using linear form of the Clausius–Clapeyron equation, the standard molar enthalpies of sublimation, at the average temperature were derived. Standard molar enthalpies and entropies of sublimation at the temperature of 298.15 K were calculated using estimated values for the heat capacity differences between the gas and the crystal phases of each compound. From the experimental values of the standard molar enthalpies of formation in the condensed phase and the values of the standard molar enthalpies of sublimation at T = 298.15 K the standard molar enthalpies of formation in the gaseous phase were calculated for the five ethyl esters of furanacrylic acid derivatives.

Due to the wide use of thermochemical characteristics of organic compounds, it is important to find the best theoretical approach for determining these properties, when experimental determination is impossible. Therefore we compared in this work the experimental data with Benson’s additive scheme [4].

For thermochemical studies we selected number of ethyl esters of furan acrylic acid derivatives:
2 Experimental

Ethyl-2-cyano-3-(furan-2-yl)-prop-2-enoate and its derivatives are obtained by the reaction shown, in Fig. 1.

Figure 1. Synthesis scheme of ethyl-2-cyano-3-(furan-2-yl)-prop-2-enoate and its derivatives

2-3 drops of piperidine were added to equimolar solution (0.1 mol) of the aldehyde (1) and cyanoacetic ester (2) in 30 ml of ethanol during boiling and mixing stage. The mixture was heated until the formation of precipitate. After cooling the reaction mixture, the precipitate was filtered, washed with ethanol and recrystallized from an ethanol-dimethylformamide mixture [5].

The structures of the substances were confirmed by IR-spectroscopy using a spectrophotometer «Specord». In the spectra of the samples absorption bands that were found that were not inherent substances of this class. The identity of the compound was confirmed by thin layer of chromatography plates Silufol UV-254.

We used samples of substances for thermochemical studies obtained after the fourth and fifth sequential re-crystallization from solvent mixture of ethanol-dimethylformamide.

The temperature dependence of the vapor pressure and enthalpies of sublimation were determined by Knudsen integral effusion method. Features of integral effusion installation are similar to those described...
in [6]. The design of the camera and membranes taken from [7] Methodology of experiments was selected in accordance with the recommendations [6].

Vacuum system of the installation has reached the pressure of 0.1 Pa for 45 ± 15s. The weight of the efunded substance $m$ was determined using analytical scales VLR-20 (± 5*10^{-6} g) as the difference of the evusion camera weight before and after the experiment. To eliminate the adsorbed moisture and volatile impurities of the sample a series of preliminary experiments were carried out at the same temperature. The experiment was finished, when the evaporation rate $m/\tau$ became constant within 1% deviation.

Reliability of the installation was tested in a series of experiments determining the temperature dependence of the vapor pressure of standard benzoic acid K-1 in the temperature range of 322.7-354.1 K using two membranes with the following diameters of holes of 2.050 mm (A) and 2.100 mm (B). Thickness of these membranes was 0.09 mm. The results of experimental determination of the temperature dependence of the vapor pressure of benzoic acid was processed by least squares method and approximated as a linear equation: $\ln P = (33.13\pm0.92)-(10535\pm89) \cdot 1/T$; the correlation coefficient $\rho=0.998$. The calculated value of the enthalpy of sublimation of benzoic acid was 87.6±0.7 kJ/mol at an average temperature $T_m=338.4$ K. This value is in concordance with the value obtained by Torez Gomez by colorimetric method at $T = 335.0$ K, $\Delta_{\text{sub}} H = 87.5 \pm 0.3$ kJ/mol [8].

Measure vapor pressure implementation of the experiments of investigated substances is similar to the experiments with benzoic acid. The results of the effusion measurements are presented in Table 1, including vapor pressure (P) of the substance in the solid aggregate state and linear equations temperature dependence of vapor pressure in the Clapeyron-Clausius equation coordinates, the value of the enthalpy of sublimation and the temperature ranges ($T_m$) that were researched. More information about the methodology and calculation of the experiment is presented in [9].

The energy of combustion of investigated substances was determined using precision calorimeter V-08-MA with an isothermal shell (± 0.003 K) and static calorimeter bomb [10]. The energy equivalent of the calorimetric system (W=15300±9 J/B) with accuracy ± 0.06 % was estimated by combustion of the reference benzoic acid grade K-1 (the major component content—99.995 % mol). Heat of combustion, considers the Jessup factor $\Delta U_{\text{jess}} = -26434.4$ J/g.

The compounds under normal conditions are in solid aggregate state. The crystalline esters were grinded in chalcedony mortar before combustion, screened and placed in platinum cup. A cotton thread, tied to the platinum wire (d = 0.1 mm) was used for the ignition. The initial pressure of the oxygen, which was previously purified from the combustible impurities, carbon dioxide and water, was equal to 3.02*10^6 Pa. 298.15 K was the initial temperature of the main period in all experiments. After each burning we conducted the quantitative analysis of the combustion products for the presence of carbon – mono and – dioxide, soot and nitric acid. The presence of carbon oxides was indicated by the Rossini method [11] within the accuracy of ± 1*10^{-4} g. Reliability of gas analysis was confirmed by a series of experiments with a reference benzoic acid. The anticipated carbon monoxide that was supposed to be formed during the combustion of products by using detector tubes within ± 1*10^{-6} g, was not encountered. The soot mass was determined by weighting the quartz cup before and after the combustion with the accuracy of ± 5*10^{-6} g. The nitric acid content was detected by titration of the liquid phase in a bomb with a 0.1 M solution of NaOH.

The investigated compounds' combustion reaction is described by equation (1):

$$C_aH_bO_cN_d + (a+b/4-c/2)O_{2g} = aCO_{2g} + (b/2)H_2O + (d/2)N_2.$$  \hspace{1cm} (1)

The internal energy of combustion in the conditions of the experiment was calculated by the formula (2):

$$-\Delta U_{298.15}^\circ = \frac{W \cdot \Delta T - q_l - q_{\text{HNO}} + q_s}{m}.$$  \hspace{1cm} (2)

where: $m$ – weight burned substance; $W$ – energy equivalent of calorimetric system; $\Delta T$ – true temperature increase; $q_l$ – amendment to the heat of combustion threads (16704.2 J/g) [12]; $q_{\text{HNO}}$ – amendment to the heat of formation of nitric acid solution (59 J/g) [12]; $q_s$ – amendment to the heat of combustion of soot (32800 J/g) [12]. More information about the methodology and calculation of the experiment is presented in [9].
Table 1. The results of effusion research of ethyl-2-cyano-3-(furan-2-yl)-prop-2-enoate and its derivatives in the crystalline state.

| Sample | T, K | m, g | τ, s | P, Pa | Sample | T, K | m, g | τ, s | P, Pa |
|--------|------|------|------|------|--------|------|------|------|------|
| Membrane (A) | Membrane (B) | Membrane (A) | Membrane (B) |
| 1 | 327.1 | 0.00250 | 3630 | 1.440 | 1 | 327.5 | 0.00360 | 3630 | 1.448 |
| | 334.1 | 0.00490 | 3640 | 2.846 | | 334.1 | 0.00550 | 3640 | 2.924 |
| 2 | 331.2 | 0.00360 | 3630 | 2.110 | 2 | 326.8 | 0.00210 | 3630 | 1.217 |
| | 335.2 | 0.00550 | 3650 | 3.214 | | 331.2 | 0.00360 | 3630 | 2.227 |

\[
\ln P(Pa) = (35.9 \pm 1.9 \cdot (12187 \pm 64)) \cdot 1/T; \Delta_{\text{mol}}H = 101.3 \pm 5.3 \text{kJ/mol}
\]

\[
\ln P(Pa) = (16201 \pm 877) \cdot 1/T; \Delta_{\text{mol}}H = 143.3 \pm 7.3 \text{kJ/mol}
\]

\[
\ln P(Pa) = (142.7 \pm 7.1) \cdot 1/T; \Delta_{\text{mol}}H = 134.7 \pm 6.2 \text{kJ/mol}
\]

The ester’s combustion energies determination results are listed in Table 2, which besides the above notation, m\textsuperscript{sub}/m\textsuperscript{cal} also specifies the combustion completion by carbon dioxide, that was obtained experimentally.

The standard enthalpies of combustion \(\Delta_c H_{298}^\circ (\text{kJ/mol})\) of investigated compounds were calculated by the average values of internal energy changes in the conditions of the experiment \(\Delta_c U\) considering the Washburn’s correction \(\pi\) [13], and the extension work correction \(\Delta nRT\).

The standard enthalpy of formation \(\Delta H_{298}^f\) was calculated using standard enthalpy of combustion and standard enthalpy of formation of combustion products (kJ/mol): \(\Delta H_{298}^f\) = 398.512 \pm 0.046; \(\Delta H_{298}^f\text{CO}_2\text{(gas)} = 398.512 \pm 0.046; \Delta H_{298}^f\text{(H}_2\text{O)_gas}) = 285.829 \pm 0.040 \cdot 1 \cdot 10^4\); \(\Delta H_{298}^f\text{(N}_2\text{gas)}) = 0 [14].

The results of calorimetric determination of the standard enthalpies of combustion and formation of these substances in the crystalline state at 298 K are shown in Table 3.
Table 2. Results of the experimental determination of combustion energies of the investigated compounds at 298.15 K.

| Sample № | m, g | ΔT, V | q, J | q_{hno3}, J | Q, J | -Δ_u, J · g⁻¹ | m^{exp}/m^{calc} |
|----------|------|-------|------|-------------|------|----------------|-----------------|
| 1        |      |       |      |             |      |               |                 |
| 0.35790  | 0.60428 | 102.0 | 14.4 | 16.7        | 25553| 1.0001        |
| 0.29219  | 0.49359 | 112.8 | 13.6 | 30.2        | 25517| 0.9990        |
| 0.29703  | 0.50070 | 74.2  | 14.2 | 26.2        | 25580| 1.0000        |
| 0.29211  | 0.49209 | 97.2  | 13.0 | 32.0        | 25522| 1.0000        |
| 0.29484  | 0.49782 | 103.3 | 14.2 | 32.5        | 25545| 0.9998        |
| 0.29739  | 0.50340 | 108.1 | 14.6 | 32.8        | 25599| 0.9999        |
| Average value: -Δ_u=25532±35             |
| 2        |      |       |      |             |      |               |                 |
| 0.29137  | 0.56740 | 89.1  | 11.8 | 26.2        | 29538| 0.957         |
| 0.29343  | 0.56931 | 71.8  | 7.1  | 29.4        | 29515| 0.955         |
| 0.29638  | 0.57713 | 93.6  | 8.3  | 23.6        | 29528| 0.959         |
| 0.29435  | 0.57230 | 88.0  | 8.4  | 32.4        | 29530| 0.944         |
| 0.28666  | 0.56426 | 90.3  | 6.2  | 36.0        | 29540| 0.966         |
| 0.29086  | 0.56831 | 75.6  | 7.5  | 25.3        | 29514| 0.952         |
| 0.29865  | 0.58046 | 81.3  | 9.6  | 27.6        | 29525| 0.954         |
| Average value: -Δ_u=29527±10             |
| 3        |      |       |      |             |      |               |                 |
| 0.29570  | 0.58978 | 75.3  | 16.2 | 36.1        | 30329| 1.000         |
| 0.28961  | 0.57877 | 88.1  | 14.8 | 28.0        | 30317| 0.994         |
| 0.29854  | 0.59654 | 91.2  | 15.6 | 30.1        | 30315| 0.990         |
| 0.29457  | 0.58699 | 69.7  | 11.8 | 23.5        | 30291| 0.994         |
| 0.29456  | 0.58852 | 90.4  | 15.9 | 25.8        | 30295| 0.999         |
| 0.29139  | 0.58110 | 70.3  | 14.2 | 18.7        | 30286| 0.989         |
| Average value: -Δ_u=30385.8±8.5           |
| 4        |      |       |      |             |      |               |                 |
| 0.29498  | 0.48009 | 60.4  | 13.6 | 25.9        | 24738| 0.958         |
| 0.29554  | 0.47231 | 72.9  | 9.4  | 27.4        | 24768| 0.997         |
| 0.29712  | 0.48444 | 55.0  | 8.9  | 15.3        | 24782| 0.997         |
| 0.29130  | 0.47627 | 91.0  | 13.6 | 23.8        | 24737| 0.978         |
| 0.32900  | 0.52161 | 68.0  | 13.6 | 34.8        | 24723| 0.979         |
| 0.29198  | 0.47700 | 84.3  | 14.6 | 30.5        | 24761| 0.994         |
| 0.30105  | 0.49123 | 74.6  | 15.3 | 21.9        | 24739| 0.990         |
| Average value: -Δ_u=24759±13              |
| 5        |      |       |      |             |      |               |                 |
| 0.28785  | 0.48716 | 80.9  | 11.2 | 28.5        | 25673| 0.993         |
| 0.29072  | 0.49416 | 88.9  | 10.0 | 24.8        | 25751| 0.993         |
| 0.29439  | 0.49926 | 91.2  | 14.3 | 35.6        | 25710| 0.992         |
| 0.31747  | 0.53703 | 75.4  | 11.8 | 28.0        | 25694| 0.994         |
| 0.29863  | 0.50571 | 84.4  | 13.0 | 29.4        | 25681| 0.994         |
| 0.29177  | 0.49432 | 89.1  | 11.2 | 42.8        | 25724| 0.996         |
| 0.30993  | 0.52582 | 85.2  | 14.2 | 29.0        | 25730| 0.994         |
Table 3. Standard enthalpy of formation and combustion in the condensed and gaseous state.

| Compound | -ΔU | -ΔnRT | ΔfH₂₉₈ | -ΔfH₂₉₈ (sol) |
|----------|-----|-------|--------|---------------|
|          | kJ/mol |       |        |               |
| I        | 4885.2 ± 6.5 | 3.7  | 0.6   | 4889.4 ± 6.5  | 331.9 ± 6.5 |
| II       | 7892.1 ± 2.7  | 5.7  | -3.1  | 7900.1 ± 2.7  | 253.2 ± 2.7 |
| III      | 8525.2 ± 2.7  | 9.9  | -6.3  | 8535.5 ± 2.7  | 297.9 ± 2.7 |
| IV       | 7728.8 ± 4.1  | 6.2  | 1.2   | 7735.0 ± 4.1  | 277.4 ± 4.1 |
| V        | 8389.0 ± 6.0  | 6.4  | 0     | 8395.6 ± 6.0  | 295.1 ± 6.0 |

3 Discussion

The thermochemical properties, identified in this work were defined at different temperatures, which are caused by the conditions of the experiment. Therefore there is a need for adjusting enthalpy of sublimation from average temperature of experiment to 298K. According to the Kirchhoff equation for conversion it is necessary to know the change in heat capacity of the appropriate phase transition. Since we do not have experimental data changes in heat capacity, it is possible to use the approximate methods of calculation. To adjust the value of the enthalpy of sublimation we used the equation proposed in [15]

$$\Delta_{sub}H^{298} = \Delta_{sub}H^{T_n} + (0,259 \pm 0,041) \cdot M \cdot (T_n - 298)$$ (3)

The values of enthalpy of formation of the compounds at 298 K in gaseous state are calculated by the equation $\Delta_fH_{298}^{(gas)} = \Delta_fH_{298}^{(sol)} + \Delta_{sub}H_{298}^{(sol)}$ and are shown in table 4.

Table 4. Enthalpic characteristics of the substances at 298K.

| Enthalpy (kJ/mol) | Substance |
|-------------------|-----------|
| -ΔfH_{298}^{(sol)} | I         |
| 331.9 ± 6.5       | II        |
| 331.9 ± 6.5       | III       |
| 331.9 ± 6.5       | IV        |
| 331.9 ± 6.5       | V         |
| ΔfH_{298}^{(gas)}  | 102.9 ± 5.6 |
| 139.8±7.0         | 148.9±8.2 |
| 154.2±8.0         | 154.2±8.0 |
| 230.0 ± 8.5       | 113.4 ± 7.5 |
| 149.0±8.6         | 123.2±9.0 |
| 155.3±10          |           |

Additive Benson’s method is one of the most common theoretical methods for calculating the enthalpy of formation of individual organic compounds in the gas phase [16]. Being studied in this article, compounds are the complex substances containing previously unknown group of additive contributions in Benson’s scheme: $C_2 - (CN)(C_3)(C)O$ and $C_3 - (C_3)(O)(C)$. We used enthalpy of formation in the gas phase of compounds I, II and group contributions for their determination referred to in [15,16] and shown in table 5.

Table 5. Used group contributions to calculate the enthalpy of formation of investigated compounds' in gaseous state.

| Group type | ΔfH_{298}, kJ/mol | Group type | ΔfH_{298}, kJ/mol |
|------------|--------------------|------------|--------------------|
| $C_2 - (C_2)(O)(H)$ | 36.61             | CO - (C_3)(O) | -140.16            |
| $C_3 - (C_3)(H)$   | 28.37             | O - (CO)(C)  | -172.80            |
| $O - (C_3)_2$     | -137.24           | C - (H)(O)(C)| -35.56             |
| $C_4 - (C_4)(O)(C_2)$ | 43.40             | C - (C)(H)   | -42.17             |
| $C_4 - (C_4)(H)(C_2)$ | 28.37             | Correction to| -25.94             |
| $C_5 - (C_5)(H)$   | 13.82             | furan cycle  |                    |
| $C_5 - (C_5)(C_4)$ | 23.76             | $C_6 - (C_6)(NO)$ | -0.52             |
| $C_6 - (C_6)(H)$   | 13.82             | $C_6 - (C_6)(N)$ | -2.09             |
| $C_4 - (CN)(C_4)(CO)$ | 158.75            | $C_6 - (C_6)(O)(C_3)$ | 59.65             |
To verify the definition of group contributions and their possible application for the calculation we had calculated enthalpy of formation in the gas phase of ethyl-2-cyano-3-[5-(4-methylphenyl)furan-2-yl]prop-2-en-0ate (III), ethyl-2-cyano-3-[5-(3-nitrophenyl)furan-2-yl]prop-2-en-0ate (IV), ethyl-2-cyano-3-[5-(4-methyl-3-nitrophenyl)furan-2-yl]prop-2-en-0ate (V) and compared them with the experimentally determined values (table 6), where $\Delta$ – is a difference between the experimental and calculated values.

**Table 6.** Experimentally determined and calculated by Benson’s additive scheme enthalpy of formation of studied ethyl ester’s in the gaseous state.

| Ester | $\Delta H^\circ_{\text{exp}}$, kJ/mol | $\Delta H^\circ_{\text{calc}}$, kJ/mol | $\Delta$, kJ/mol |
|-------|-----------------------------------|-----------------------------------|-----------------|
| III   | 149.00                            | 146.87                            | 2.13            |
| IV    | 123.20                            | 127.40                            | 4.20            |
| V     | 155.30                            | 161.21                            | 5.91            |

4 Conclusions

A combined experimental and theoretical study has been carried out to obtain the standard molar enthalpies of formation in the gas-phase at 298 K for five ethyl esters of furanacrylic acid derivatives. From the experimental data for ethyl-2-cyano-3-(furan-2-yl)-prop-2-en-0ate derivatives enthalpies of combustion, and sublimation were determined. Combining these two quantities, the standard molar enthalpies of formation in the gaseous phase at 298 K were obtained. From the obtained values two new increments filling Benson’s additive-group scheme were determined. Since, the Benson group method yields estimates of standard molar enthalpies of formation in the crystalline and gas phase are very close to the experimental values, we may conclude that the new increments can be accepted with confidence for the estimation of formation enthalpies for the compounds that are not studied experimentally.

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