



J. Serb. Chem. Soc. 84 (5) 477–481 (2019)
JSCS–5200

SHORT COMMUNICATION

Empirical method for predicting the enthalpy changes of combustion of amides

ALMA K. RYSKALIYEVA*, MURAT E. BALTABAYEV and
KURMANKUL T. ABAEVA

*Department of Plant Protection and Quarantine, Kazakh National Agrarian University,
8 Abay av., Almaty 050010, Kazakhstan*

(Received 9 August, revised 17 October, accepted 6 November 2018)

Abstract: The enthalpy change of combustion is one of the basic thermochemical characteristics of an organic compound, indicating the amount of heat produced in the complete combustion of the substance. The enthalpy changes of combustion of many organic compounds have been experimentally determined. Hitherto, the existing empirical approaches have aimed at calculating the combustion enthalpy change of individual classes only, which do not always satisfactorily agree with the experimental results. Therefore, the method of correlation–regression analysis is proposed herein to establish the combustion enthalpy changes of previously unexplored compounds. As is known, a linear relationship between two characteristics is possible only if both of them obey the principle of additivity, *i.e.*, in a homologous series of organic compounds with increasing number of CH₂-groups, the value of additive characteristic (for example, the enthalpy change of vaporization) should increase by a certain constant amount.

Keywords: enthalpy change of combustion; amides; thermochemistry.

INTRODUCTION

Correlation–regression analysis of experimental data is widely applied in all sections of chemistry to quantitatively describe chemical phenomena, systematize facts and perform calculations. In particular, correlation–regression analysis of thermochemical data enables convenient and reliable formulas for practical calculations to be obtained.^{1,2} Herein, a correlation analysis of the results of experimental thermochemical studies on the combustion of amides was conducted, which would allow regularity in the values of the obtained combustion enthalpy changes to be revealed.

* Corresponding author. E-mail: aryskalieva@mail.ru
<https://doi.org/10.2298/JSC180809094R>

EXPERIMENTAL

An industrial calorimeter B-08-MA with an isothermal shell and a stationary self-packing calorimetric bomb ($V_{\text{int.}} = 325 \text{ cm}^3$) equipped with two valves (for input and output of gases) was used to determine the enthalpy changes of combustion of the studied compounds. The error in the measuring of the calorimeter B-08-MA is $\pm 0.1 \%$, which is clearly insufficient for precision measurements. Therefore, in order to improve the accuracy of the determination of the energy of combustion of the substances, some parts of the calorimeter were refined. In particular, a system for thermostating the shell, an oxygen purification system, a system for sample ignition, a calorimetric vessel, and a calorimetric bomb were modified. The changes to the calorimeter enabled the accuracy of the obtained thermochemical values to be improved to $\pm 0.01 \%$.

The test samples of amides, anilides and amidic acid were burned as tablets with or without an auxiliary substance in the form of a special polyethylene film. The masses of the combustible samples and polyethylene were determined on a microbalance with an accuracy of $\pm 2 \times 10^{-5} \text{ g}$. Moreover, the amount of substance was chosen as recommended in the reference literature.³

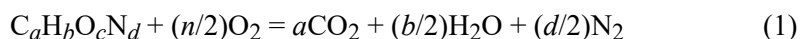
After the completion of the experiment, the combustion gases were analyzed for their CO_2 content by the Rossini method (accuracy $\pm 0.05 \%$).⁴ The analysis for the CO content was realized with the help of indicator tubes (sensitivity $6 \times 10^{-6} \text{ kg L}^{-1}$). The experimental values of the enthalpies of combustion of the studied amides are presented in Table I.

TABLE I. The experimental and calculated values of the combustion enthalpy changes of the studied amides

Compound	$-\Delta_c H_{\text{exp.}} / \text{kJ mol}^{-1}$	n	$-\Delta_c H_{\text{calc.}} / \text{kJ mol}^{-1}$	$\varepsilon / \%$
<i>N,N</i> -Methylacetylcarbamide	2154.32	10	2180	1.2
Oxamide	851.70	4	872	2.3
α -Cyanacetamide	1565.43	7	1526	2.5
α -Phenylacetamide	4210.40	19.5	4251	0.9
Valeramid	3140.62	14.5	3161	0.6
Salicylamide	3352.32	15.5	3379	0.8
Nicotinamide	3083.78	14	3052	1.0
<i>N,N</i> -Dimethylbenzamide	4959.91	22.5	4905	1.1

RESULTS AND DISCUSSION

Inside the calorimeter, the process of complete combustion of amides occurs according to the general equation:



The enthalpy changes of combustion of the studied amides and the number of oxygen atoms, $n = 2a + b/2 - c$, required for the complete combustion of one mole of the studied amide are presented in Table I and a simple regularity that relates these quantities to each other was found:

$$-\Delta_c H = 218n \quad (2)$$

The linear nature of this relationship was confirmed by the value of the correlation coefficient, which was 0.992. The observed dependence enables the clarification of the physicochemical meaning of the found correlation (2) and an examination of the accuracy of the predictive calculations based on it (Table I).

It is possible to assess qualitatively the degree of reliability of the proposed calculation for enthalpy change of combustion of amides from the relation (2) from Table I, which presents the values established experimentally and the calculated values.

The greater the number of CH groups in the amides, the greater will be the quantity of carbon dioxide and water formed because of combustion, and the greater will be the number of oxygen atoms n necessary for their formation. If the process of complete combustion of amides would be accompanied by the formation of nitrogen oxides, it could similarly be assumed that the greater the number of nitro groups in the amide formula, the greater would be the amount of oxygen required for the combustion of the amide. As can be seen from the general Eq. (1) for the combustion of amides, this was not the case. Therefore, according to Table I, it is easy to determine that with increasing number of nitro groups in the amide formula, the relative deviation of the predicted values from the experimental values of the enthalpy change of combustion increases. However, on the other hand, it can be seen from Table I that the relative deviations of the calculated values of the enthalpy changes of combustion of amides from the experimental values do not exceed 2.5 %, which indicates a sufficient reliability of the prediction method.

The logic of the reasoning and the good agreement between the predicted and experimental values of combustion enthalpy changes (Table I) allows the assumption that the mole fraction of nitrogen atoms in the amide formula might serve as a certain quantitative limiting factor, which would indicate the upper margins of the relative deviation of the predicted and experimental values of the enthalpy change of combustion.

In this regard, the correlation coefficient between the relative deviation and X_N , the mole fraction of nitrogen atoms in the amide, was found to be rather high and equal to 0.929. Thus, based on the regression analysis, the following relationship was obtained:

$$|\varepsilon| = 12X_N \quad (3)$$

Based on this relationship, it is possible to estimate the expected maximum errors of the predicted values of the enthalpy change of combustion of amides calculated according to formula (2).

In accordance with the calculated formulas (2) and (3), the enthalpy changes of combustion and their maximum expected errors of amides were calculated and compared with the thermochemical properties experimentally studied by other

authors. A comparison of the calculated and experimental values is given in Table II.

Table II. Comparison of the literature and calculated values of $\Delta_c H$ and $|\varepsilon|$ of some amides

Compound	$-\Delta_c H_{\text{exp.}} / \text{kJ mol}^{-1}$	n	$-\Delta_c H_{\text{calc.}} / \text{kJ mol}^{-1}$	$\varepsilon_{\text{exp}} / \varepsilon_{\text{theor}}$
1-Methylcarbamide	1311.74	6	1308	-0.3/2.1
Ethylcarbamide	1966.10	9	1962	-0.2/2.0
Isopropylcarbamide	2613.70	12	2616	0.09/1.4
<i>tert</i> -Butylcarbamide	3267.80	15	3270	0.07/1.2
Acetamide	1186.03	5.5	1199	1.1/1.3

As can be seen from Table II, the values given in the literature and the calculated values are in a good agreement with each other. The table also shows that the relative deviations of the predicted values from the experimental values do not exceed the upper margin of the relative deviations calculated by formula (3).

CONCLUSIONS

The thermochemical properties of amides should be known when studying the mechanism of chemical reactions and thermodynamic equilibrium for the purposeful synthesis of amides with given properties and when developing optimal technological processes for the industrial production of these compounds.

The good agreement between the predicted values of the enthalpy change of combustion of amides calculated by correlation (2) and the experimental values suggests that researchers can use the methods proposed above to predict the enthalpy changes of combustion of amides for which there is no reliable experimental data, and to predict the expected marginal error in calculating these quantities. Technologists can also use these methods for performing engineering calculations.

The effectiveness of correlations (2) and (3), despite their simplicity, suggests that the next stage of study can find out a more general relationship that would reflect a correlational dependency of the enthalpy changes of combustion on two variables – the number of oxygen atoms and the mole fraction of nitrogen atoms in an amide. Thus, the potential relation would combine formulas (2) and (3).

ИЗВОД

ЕМПИРИЈСКИ МОДЕЛ ЗА ПРЕДВИЃАЊЕ ПРОМЕНА ЕНТАЛПИЈА САГОРЕВАЊА АМИДА

ALMA K. RYSKALIYEVA, MURAT E. BALTABAYEV и KURMANKUL T. ABAEVA

Department of Plant Protection and Quarantine, Kazakh National Agrarian University, 8 Abay av., Almaty 050010, Kazakhstan

Промена енталпије сагоревања је једна од основних термодинамичких карактеристика органских једињења која представља количину топлоте произведене при комплетном сагоревању супстанције. Промена енталпије сагоревања великог броја органских једињења су одређене експериментално. Постојећи емпиријски приступи су имали за циљ

израчунавање промене енталпије сагоревања само за индивидуалне класе, што се не слаже увек на задовољавајући начин са експерименталним подацима. Због тога је у овом раду предложен метод корелационо–регресионе анализе за одређивање промене енталпије сагоревања једињења за која та вредност није одређена. Као што је познато, линеарна веза између две величине је могућа само онда када обе величине задовољавају услов адитивности, тј. у хомологим серијама органских једињења код којих расте број CH_2 група вредност адитивних карактеристика (на пример, промена енталпије испаравања) треба да се повећава за константан износ.

(Примљено 9. августа, ревидирано 17 октобра, прихваћено 6. новембра 2018)

REFERENCES

1. E. V. Sagadeev, V. V. Sagadeev, *High Temp.* **4** (2002) 581 (<https://doi.org/10.1023/A:1019663013424>)
2. A. K. Ryskaliyeva, M. E. Baltabayev, A. M. Zhubatova, *Acta Chim. Slov.* **65** (2018) 127 (<https://doi.org/10.17344/acsi.2017.3683>)
3. V. P. Kolesov, *Osnovy termokhimii (Fundamentals of thermochemistry)*, MSU, Moscow, 1996, p. 205 (ISBN 5211033795)
4. F. D. Rossini, *Experimental thermochemistry: measurement of heats of reaction*, Interscience Publishers, New York, 1956, p. 326 (ISBN 9110141278).