

## Regularities of Enthalpies of Combustion of Nitrogen-Containing Organic Compounds

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**Summary:** In the following work, the enthalpies of combustion of 16 nitrogen-containing organic compounds - amides and anilides were experimentally determined using the method of bomb calorimetry. The regularities of the course of the change in the enthalpies of combustion of these compounds have been found. Thus, the analysis of the obtained data revealed the presence of two correlation dependences for these substances. The established correlations indicate the dependence of the numerical values of enthalpies of combustion on stoichiometric amount of oxygen in chemical reaction equations for the complete combustion of amides and anilides. To evaluate the efficiency of new correlations, they were tested on experimental data obtained by the other authors on the example of combustion of other 9 amides and 7 anilides. For these compounds, the experimental values of enthalpies of combustion and the calculated values do not diverge by more than 10%. This indicates the efficiency of the proposed ratios for predicting enthalpies of combustion of not yet studied amides and anilides.

**Keywords:** Enthalpy of combustion; Nitrogen-containing organic compounds; Predictive calculations.

### Introduction

Among nitrogen-containing organic compounds, carbamide and its alkyl-substituted derivatives are widely used in crop farming, animal husbandry, pharmacology, and in the chemical industry. Therefore, it is necessary to replenish the bank of available experimental data on enthalpies of combustion and formation of these substances systematically [1-3, 5-10] to carry out chemical-technological calculations. However, the experimental data on many alkyl-substituted carbamide derivatives is either unknown or difficult to obtain. In this regard, the identification of the patterns that link the thermochemical properties of alkyl-substituted urea derivatives with their structure or stoichiometry of chemical reaction equations to develop the methods for predictive calculations of enthalpies of combustion of unexplored compounds becomes a rather interesting direction of research.

### Experimental

The technique and procedures of the experimental work for determination the enthalpies of combustion of amides and anilides by the method of bomb calorimetry as well as the origin and purity of the compounds used in the experiment are described in our work elsewhere, in which we conducted the similar experiment with the same materials [4].

The enthalpies of combustion ( $\Delta_c H^0$ ) and the calculated values of the enthalpies of formation

( $\Delta_f H^0$ ) for the amides and anilides under study are presented in Table-1.

Table-1: Standard enthalpies of combustion and formation of amides and anilides.

Compound	$-\Delta_c H^0$ , kJ·mol <sup>-1</sup>	$-\Delta_f H^0$ , kJ·mol <sup>-1</sup>
N, N-methylacetylcarbamide	2154.32±2.28	563.10±2.28
methylacetylcarbamide		
Oxamide	851.70±2.27	507.01±2.27
$\alpha$ -cyanoacetamide	1565.43±2.52	186.80±2.52
N, N-dimethylacetamide	2598.04±37.41	282.30±37.41
$\alpha$ -phenylacetamide	4210.40±3.79	224.02±3.79
Propionamide	3550.10±0.82	291.37±0.82
Valeramide	3140.62±0.84	329.04±0.84
Isovaleramide	3149.68±1.73	390.02±1.73
Salicylamide	3352.32±2.21	402.68±2.21
Nicotinamide	3083.78±1.69	131.85±1.69
N, N-dimethylbenzamide	4959.91±1.02	153.87±1.02
Formanilide	3591.40±1.72	177.23±1.72
2,4-dimethylacetanilide	5501.93±0.83	291.20±0.83
P-aminoacetanilide	4341.30±2.28	267.10±2.28
Benzanilide	6576.05±4.68	111.80±4.68
Salicylicanilide	6379.64±3.01	308.21±3.01

### Results and Discussion

We analyzed the experimental values obtained for the enthalpies of combustion of amides and the stoichiometry of the equations of chemical reactions of combustion. The combustion of amides in the calorimeter proceeds according to the following reaction equation:



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Table-2: A comparison of enthalpies of combustion and oxygen consumption for combustion of one mole of combustible substance

Compound	Combustion reaction	Number of oxygen atoms, mole	$-\Delta_c H_{exp}$ , kJ·mol <sup>-1</sup>
Oxamide	$(CONH_2)_{2(c)} + 2O_{2(g)} \rightarrow 2CO_{2(g)} + N_{2(g)} + 2H_2O_{(l)}$	4.0	851.70
Valeramide	$CH_3(CH_2)_3CONH_{2(c)} + (29/4)O_{2(g)} \rightarrow 5CO_{2(g)} + (1/2)N_{2(g)} + (11/2)H_2O_{(l)}$	14.5	3140.62
Salicylanilide	$HOC_6H_4CONHC_6H_5(c) + (59/4)O_{2(g)} \rightarrow 13CO_{2(g)} + (1/2)N_{2(g)} + (11/2)H_2O_{(l)}$	29.5	6379.64

For the complete combustion of one mole of an amide,  $n = (2c + d / 2 - f)$  moles of oxygen are necessary. The comparison of the values of enthalpies of combustion  $\Delta_c H_i$  and the amount of oxygen  $n_i$  required for the combustion of one mole of amide in Table-2 demonstrates the presence of a simple pattern - the greater the cost of oxygen for the complete combustion of one mole of a combustible substance, the greater the absolute value of the enthalpy of combustion. As is known, the degree of linearity of the correlative conjunction is determined by the correlation coefficient R between  $\Delta_c H_i$  and  $n_i$ , where  $i = 1, 2, \dots, N$ ; N is the number of points pairs ( $\Delta_c H_i, n_i$ ).

Separate consideration of amides and anilides gave the maximum values of the correlation coefficients which indicated the existence of two linear relationships that describe the dependence of the enthalpies of combustion for these classes of substances on the number of oxygen atoms (n):

$$-\Delta_c H = a \cdot n + b \quad (1)$$

The coefficients a and b are determined by the method of least squares, wherein the estimation of dispersion  $\sigma_0$  is determined by the equation:

$$\sigma_0^2 = \frac{1}{(N-2)} \left( -\sum_{i=1}^N \Delta_c H_i^2 + a \sum_{i=1}^N \Delta_c H_i + b \sum_{i=1}^N n_i \Delta_c H_i \right) \quad (2)$$

As a result, the following linear correlations have been obtained

$$\text{For amides: } \Delta_c H = 218 \cdot n \text{ (kJ} \cdot \text{mol}^{-1}) \quad (3)$$

$$\text{For anilides: } \Delta_c H = 212 \cdot n + 92 \text{ (kJ} \cdot \text{mol}^{-1}) \quad (4)$$

The values of the correlation and dispersion coefficients as well as the numerical values of the enthalpies of combustion  $\Delta_c H$  calculated with help of new correlations (3), (4) are presented in Table-3.

As can be seen from the table, the correlation coefficients for amides and anilides indicate a distinct linear correlation ( $R \geq 0.75$ ). The value of the dispersion  $\sigma_0$  for amides is higher than the dispersion of anilides, which is explained by the

sample size, in which 11 pairs of points ( $\Delta_c H_i, n_i$ ) were taken for amides and 5 pairs of points were taken for the anilides. Nevertheless, the relative error in  $\Delta_c H$  calculation does not exceed 2.5% for amides and 0.5% for anilides.

It can be seen from Table-3 that the relative deviation of the calculated values of combustion enthalpies from the experimental values decreases in the case when alkyl groups are sufficiently represented in the amide structure. In other words, the more carbon and hydrogen in the gross formula of the combustible substance  $C_c H_d O_f N_g$ , the smaller is the numerical value of the relative error:

$$\varepsilon \sim (c+d)^{-1} \quad (5)$$

Table-3 shows that the average value of  $\varepsilon$  for anilides (0.2) is less than the average value of  $\varepsilon$  for amides (1.3). This corresponds to a different content of carbon and hydrogen in the chemical composition of amides and anilides.

We also revealed the following regularity: the relative deviation of  $\varepsilon$  increases with the increase in the number of nitrogen atoms in the formula of the combustible substance  $C_c H_d O_f N_g$ :

$$\varepsilon \sim g \quad (6)$$

From the relations (5) and (6) we can obtain the following proportionality:

$$\varepsilon \sim d/(c+d) \quad (7)$$

where d - is the number of nitrogen atoms, c - is the number of carbon atoms, d - is the number of hydrogen atoms in the nitrogen-containing substance formula. For alkyl-substituted carbamide derivatives, this means that the accuracy of the predictive calculation of combustion enthalpies depends on the ratio of nitro groups and alkyl groups in the formula of combustible substance.

Here we can say that the search for a regular quantitative relationship between  $\varepsilon$  and the content of carbon, hydrogen, and nitrogen in the formula of nitrogen-containing substance is an interesting task for the future research. The solution of this problem would allow us to predict the accuracy of calculations using correlations (3) and (4).

Table-3: A comparison of the experimental and calculated values of  $\Delta_c H$  of amides and anilides.

Compound	$-\Delta_c H_{exp.}, kJ \cdot mol^{-1}$	n - number of oxygen atoms	$-\Delta_c H_{cal.}, kJ \cdot mol^{-1}$	Relative error $\epsilon, \%$
for amides: $-\Delta_c H = 218n$ ; ( $\sigma_o = 46, R = 0,99$ )				
N, N-dimethylbenzamide	4959.91	22.5	4905.0	1.1
$\alpha$ -phenylacetamide	4210.40	19.5	4251.0	0.9
Salicylamide	3352.32	15.5	3379.0	0.8
Valeramide	3140.62	14.5	3161.0	0.6
Nicotinamide	3083.78	14.0	3052.0	1.0
N, N-methylacetylcarbamide	2154.32	10.0	2180.0	1.2
$\alpha$ -cyanoacetamide	1565.43	7.0	1526.0	2.5
Oxamide	851.70	4.0	872.0	2.3
for anilides: $-\Delta_c H = 92 + 212n$ ; ( $\sigma_o = 4.5; R = 0.99$ )				
Benzanilide	6576.05	30.5	6558.0	0.3
Salicylicanilide	6379.64	29.5	6346.0	0.5
2,4-dimethylacetanilide	5501.93	25.5	5498.0	0.07
o-methylacetanilide	4871.35	22.5	4862.0	0.2
p-aminoacetanilide	4341.30	20.0	4332.0	0.2
Formanilide	3591.40	16.5	3590.0	0.04

Table-4: A comparison of the literary and calculated values of enthalpies of combustion  $\Delta_c H$ .

Compound	$-\Delta_c H_{exp.}, kJ \cdot mol^{-1}$	n - number of oxygen atoms	$-\Delta_c H_{cal.}, kJ \cdot mol^{-1}$	Relative error $\epsilon, \%$
for amides: $-\Delta_c H = 218n$				
Benzamide [5]	3552.20	16.5	3597.0	1.26
Tretbutylcarbamide [6]	3267.80	15.0	3270.0	0.07
Isopropylcarbamide [5]	2613.70	12.0	2616.0	0.09
Ethyl carbamide [5]	1966.10	9.0	1962.0	0.21
1-methylcarbamide [5]	1311.74	6.0	1308.0	0.29
Acetamide [7]	1185.18	5.5	1199.0	1.17
Biuret [5]	907.91	4.5	981.0	8.05
Carbamide [5]	632.06	3.0	654.0	3.47
N, N-dimethylformamide [8]	564.54	2.5	545.0	3.46
for anilides: $-\Delta_c H = 92 + 212n$				
2-Ethylacetanilide [9]	5518.60	25.5	5498.0	0.37
2-Methoxyacetanilide [9]	4779.60	21.5	4650.0	2.71
4-Methoxyacetanilide [9]	4718.92	21.5	4650.0	1.46
Acetanilide [10]	4224.84	19.5	4226.0	0.03
2-Hydroxyacetanilide [9]	4015.84	18.5	4014.0	0.05
2-Nitroacetanilide [9]	4067.43	17.0	3696.0	9.13
3-Nitroacetanilide [9]	4012.10	17.0	3696.0	7.88

At this stage, it is important to evaluate the efficiency of these correlations for describing the experimental data of other authors. To this end, the enthalpies of combustion of 9 amides and 7 anilides were calculated with help of correlations (3) and (4) to compare them with the experimental data obtained by other authors (Table-4).

As can be seen from Table-4, the experimental values of the enthalpies of combustion and their calculated values do not diverge by more than 10%. The regularities (5) and (6) are also present in this table and more noticeable numerically.

For further research, it is important to understand that the linear correlations (3), (4) and the proportionality relation (7) give a reason to assume that there is a more general dependence of enthalpies of combustion on two variables: 1) the number of oxygen atoms in the reaction equation and 2) the ratio of nitro- and alkyl groups in the formula of nitrogen-containing compound.

## Conclusion

By the method of bomb calorimetry, the enthalpies of combustion of 11 amides and 5 anilides have been experimentally determined. Their standard

enthalpies of formation have been calculated. New linear relationships connecting the enthalpies of combustion of these compounds with the number of oxygen atoms spent for complete combustion of one mole of the nitrogen-containing organic compound have been found.

The relative deviation of the experimental values from the values calculated from new ratios does not exceed 10%, which agrees with the generally accepted accuracy for Lauthier-Karapetyants correlations [11].

Consequently, these relations are suitable for predictive calculations of the numerical values of the enthalpies of combustion of experimentally unexplored amides and anilides. In this case, the best predictions can be expected from the combustion of compounds containing more alkyl groups and less nitro groups.

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