

Dedicated to Professor Dr. ALEXANDRU T.
BALABAN, member of the Roumanian Academy
on the occasion of his 75th anniversary

ENTHALPIES OF COMBUSTION AND FORMATION OF ISOMERS OF THE AMINO-BENZOIC ACID

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The energies of combustion of the *o*-, *m*- and *p*- isomers of the amino-benzoic acid in the crystalline state were measured in a static bomb adiabatic calorimeter, in pure oxygen at 3040 kPa. Corrections were made for the heats due to the ignition of sample and for the nitric acid formation. The derived enthalpies of formation for the isomers are: $\Delta_f H_{cr}^0 = -399.0 \pm 3$ kJ/mol for *o*-amino-benzoic acid, $\Delta_f H_{cr}^0 = -416.6 \pm 4.1$ kJ/mol for *m*-amino-benzoic acid and $\Delta_f H_{cr}^0 = -408.7 \pm 2.3$ kJ/mol for *p*-amino-benzoic acid, respectively. Their resonance energies were calculated and correlated with the corresponding molecular structures.

INTRODUCTION

The present paper continues our research concerning the thermochemical properties of nitrogen containing organic compounds, mainly amino acids.¹⁻³

Although not directly involved in the protein structure, amino-benzoic acids are compounds of important biological activity. They are also involved in the synthesis of some drugs, dyestuffs, aromatization agents, preservatives.

In particular, *p*-amino-benzoic acid, part of the folic acid, is named vitamin B_x and although a non-protein amino acid, it is widespread in nature. Its role in maintaining the healthy state of hair and skin is well known.

o-amino-benzoic acid, known also as anthranilic acid or L vitamin, is an intermediary in the synthesis of tryptophan. It plays an important role in lactation. It is used in the production of perfumes, dyestuffs, drugs, as absorbent of UV radiations and as corrosion inhibitor.

The ethyl-ester of *m*-amino-benzoic acid is used as anesthetic.

Knowing the amino-acid properties is important for a better understanding of the protein structure, serving as model compounds in the study of the latter.

In this study we follow the influence of the reciprocal position of the two substituents, upon the thermochemical properties of the three isomers – enthalpies of formation, resonance energies and consequently the variation of their stability according to their structure.

EXPERIMENTAL

The samples of benzoic acid isomers were Merck reagents of over 98.9 % purity.

Apparatus and experimental procedures

The adiabatic calorimeter with static bomb and the basic experimental procedures used in this investigation have been already described.² The calorimeter is of the Parr Instruments type, locally built. It is provided with an electronic system, which allows it to

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work in adiabatic conditions. The calorimetric bomb is a cylinder, with a volume of about 300 mL, made of stainless steel, as well as its accessories. The temperature rise was measured by means of a Beckmann thermometer; the temperature rise due to the combustion reaction is considered as the difference between the final and initial temperature values, when the difference between two consecutive readings is about 0.002°C.

The initial temperature was $25.0 \pm 0.2^\circ\text{C}$ and the initial pressure was 3040 kPa.

The samples to be burned were pressed into pellets and weighed with an accuracy of 0.01 mg. The pellet was placed in the bomb crucible, in the proximity of the fuse used for ignition. The combustion was run in the presence of a cotton fuse, as an auxiliary of combustion, if necessary. The bomb was flushed with purified oxygen for three minutes, then sealed and filled with oxygen at the initial pressure mentioned above. After combustion, the gas mixture from the bomb was evacuated. The walls and fittings of the bomb were washed with bidistilled water and the resulted solution was saved in a 200 mL flask.

Calibration

The calorimeter constant was determined by means of benzoic acid combustion (standard reference material 39I from NIST). The considered certified value of energy of combustion of benzoic acid is $26454 \pm 3.7 \text{ J/g}$. The calorimeter constant was calculated from the results of at least ten combustion runs, resulting in a value of $8901 \pm 2.8 \text{ J/K}$.

Analysis of the final solution

Three samples of solution of 50 mL were titrated separately, with 0.1 N NaOH solutions, using methyl orange as indicator. The mean value of three titrations was used for the calculation of the amount of nitric acid resulting from combustion (about 20% from the total nitrogen). The heat due to nitric acid formation was obtained using the value of the enthalpy of formation of nitric acid - $\Delta_f H_{\text{HNO}_3, \text{aq}} = -58.8 \text{ kJ/mol}$.⁸

RESULTS

Combustion energy of the samples

The determination of combustion energies for the samples was done in the same way as for the calibration of the calorimeter. The results are given in Tables 1-3 for the *o*-, *m*- and *p*-isomers. The tables entries include: *m*, mass (g) of the burned substance, $\Delta\theta$, temperature rise (K), *Q*, total energy observed (J), q_i , energy (J), used to ignite the sample (calculated from mass of the fire and $\Delta_f H_{\text{Fe}_2\text{O}_3} = 6.688 \text{ kJ/g}$), q_b , energy of burned cotton (J) (calculated from the mass of cotton and $\Delta_c H_{\text{cotton}} = 16137 \text{ J/g}$)⁴, q_{HNO_3} , energy of nitric acid formation (J), ΔU^{exp} energy of combustion of sample (J/g), ΔU^{exp} molar energy of combustion (in J/mol), $\Delta_c U^0$ standard molar energy of combustion (J/mol).

Table 1

Combustion data of 2-aminobenzoic acid

<i>m</i> (g)	ΔT (K)	<i>Q</i> (J)	q_i (J)	q_b (J)	q_n (J)	$-\Delta_c u^{\text{exp}}$ (J/g)	$-\Delta_c U^{\text{exp}}$ (kJ/mol)	$-\Delta_c U^0$ (kJ/mol)
0.67937	1.953	17384	50	693	25	24455	3353.7	3353.1
0.89816	2.565	22831	52	742	60	24468	3355.6	3355.0
0.78948	2.260	20117	52	710	28	24478	3356.9	3356.3
0.86329	2.465	21941	53	682	46	24510	3361.3	3360.7
0.80745	2.307	21096	54	691	35	24467	3355.3	3354.7
0.79826	2.276	20589	52	657	33	24449	3353.0	3352.4

Mean value - 3355.4 kJ/mol
Standard deviation $\pm 3.0 \text{ kJ/mol}$

In order to bring the experimental values of energy of combustion to the standard state ($T = 298.15 \text{ K}$ and $P = 1001.3 \text{ kPa}$), corrections were made with the Washburn equation⁵ recommended in the case of compounds with carbon, hydrogen and oxygen of $\text{C}_a\text{H}_b\text{O}_c$ general formula :

$$\Pi \% = \frac{-0.3aP_{\text{initial}}}{-\Delta U^{\text{exp}}} \left[1 - \frac{1.1(b-2c)}{4a} + \frac{2}{P_{\text{initial}}} \right] \quad (1)$$

where P stands for the initial oxygen pressure and $-\Delta U^{\text{exp}}$ for the experimental energy of combustion, a, b, and c being the atom numbers of carbon, hydrogen and oxygen from the chemical formula of the compound, respectively. Π is calculated in percents from the experimental value. The above equation applies fairly well in the case of nitrogen compounds as well.⁶

The relative error in the determination of the heats of combustion was better than 1%.

Table 2

Combustion data of 3-aminobenzoic acid

m (g)	ΔT (K)	Q (J)	q_i (J)	q_b (J)	q_n (J)	$-\Delta_c u^{\text{exp}}$ (J/g)	$-\Delta_c U^{\text{exp}}$ (kJ/mol)	$-\Delta_c U^0$ (kJ/mol)
0.66112	1.878	16716	50	555	21	24307	3333.4	3332.8
0.63749	1.828	16271	55	605	20	24345	3338.6	3338.0
0.64455	1.831	16298	49	553	27	24309	3333.7	3333.1
0.85310	2.423	21567	52	688	32	24375	3342.7	3342.1
0.74378	2.118	18853	52	641	65	24327	3336.3	3335.7
0.67934	1.949	17348	53	725	28	24349	3339.2	3338.6
0.67115	1.920	17090	52	645	27	24384	3344.0	3343.4

Mean value - 3337.7 kJ/mol
Standard deviation \pm 4.12 kJ/mol

Table 3

Combustion data of 4-aminobenzoic acid

m (g)	ΔT (K)	Q (J)	q_i (J)	q_b (J)	q_n (J)	$-\Delta u^{\text{exp}}$ (J/g)	$-\Delta U^{\text{exp}}$ (kJ/mol)	$-\Delta U^0$ (kJ/mol)
0.73677	2.096	18656.7	51	586	32	24412.54	3347.93	3347.33
0.65738	1.875	16689.58	49	574	32	24385.76	3344.26	3343.66
0.78401	2.229	19840.57	53	645	33	24372.82	3342.48	3341.88
0.88391	2.513	22368.49	51.57	699	57.89	24391.56	3345.06	3344.46
0.70869	2.028	18051.45	51.7	658.5	38.3	24415.12	3348.29	3347.69
0.94558	2.682	23872.72	51.3	684.8	48.9	24416.32	3348.45	3347.85
0.62501	1.763	15692.65	53.9	564.6	28	24392.00	3345.12	3344.52

Mean value - 3345.6 kJ/mol
Standard deviation \pm 2.27 kJ/mol

Standard enthalpies of combustion and formation

The standard combustion enthalpies of the samples were calculated using the following equation:

$$\Delta_c H_{(s)}^0 = \Delta_c U_{(s)}^0 + \Delta n RT \quad (2)$$

$$\Delta n = \sum n_{\text{gas, products}} - \sum n_{\text{gas, reactants}}$$

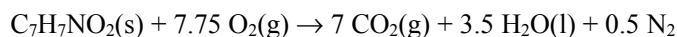
Δn is the change in the gas mole number, in the combustion reaction. $R = 8.314 \text{ J/mol}\cdot\text{K}$; $T = 298.15 \text{ K}$.

Table 4

Combustion and formation enthalpies of the solid state isomers of the amino-benzoic acid

Isomer	$-\Delta_c H^0$ (kJ/mol)	$-\Delta_f H^0$ (kJ/mol)	Literature ^{9,10}	
			$-\Delta_c H^0$ (kJ/mol)	$-\Delta_f H^0$ (kJ/mol)
<i>ortho</i>	3356.0 ± 3.0	399.0 ± 3.0	3353.8 ± 0.8	401.1 ± 1.2
			3354.0 ± 0.8	401.0 ± 0.8
<i>meta</i>	3338.3 ± 4.1	416.6 ± 4.1	3337.6 ± 1.3	417.3 ± 1.6
			3344.0 ± 0.4	411.0 ± 0.4
<i>para</i>	3346.3 ± 2.3	408.7 ± 2.3	3345.0 ± 1.5	410.0 ± 1.7
			3342.0 ± 0.4	413.0 ± 0.4

The combustion experimental data are given for the following reaction, the same for all three isomers:



$$\Delta n = -0.25$$

For calculating the formation enthalpies of the investigated compounds, the following values were considered: $\Delta_f H_{\text{CO}_2}^0(\text{g}) = -393.51 \pm 0.13 \text{ kJ/mol}$, $\Delta_f H_{\text{H}_2\text{O}}^0(\text{l}) = -285.83 \pm 0.042 \text{ kJ/mol}$.⁷

DISCUSSION

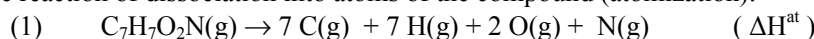
The enthalpies of combustion and formation of the three isomers of amino-benzoic acid were reported long time ago, by Nabavian and co-workers⁹ and by Lebedeva and co-workers¹⁰. Our experimental values for the enthalpies of combustion are larger in absolute value than those of the French group⁹, but the order of the values for the three isomers is the same (decreasing values of $\Delta_c H^0$ in the order *o*-, *p*-, *m*-). However the differences between our values and those of reference⁹ are lower than the cumulated uncertainties. Obviously, our enthalpies of formation are less negative than those reported by the above mentioned authors.

The calculation of resonance energies

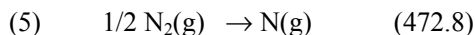
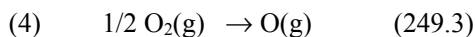
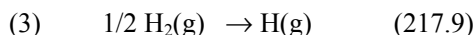
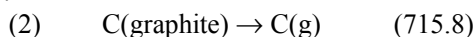
The stabilization of the investigated molecules by resonance was evaluated by means of their resonance energies.

The resonance energy, defined as the energy difference between the systems of delocalized and localized π electrons was calculated referring to contributions of the bonds contained by the molecules.⁸

Consider the reaction of dissociation into atoms of the compound (atomization):



The energy of atomization ΔH^{at} is obtained from the enthalpy of formation reaction and the thermal effects of the following reactions:



(all values in kJ/mol)

Combination of chemical equations 1-5 yields:

$$\Delta H^{\text{at}}(\text{exp}) = 7511.2 - \Delta_f H^0(\text{g}) \text{ kJ/mol} \quad (3)$$

On the other hand ΔH^{at} , the atomization energy, is expressed as the sum of the bond energies from the molecule:

$$\Delta H^{\text{at}}(\text{calc}) = - \sum D_i(\text{A}-\text{B}) \quad (4)$$

The bond energies refer to molecules in the gaseous state, so that the energies $\Delta H^{\text{at}}(\text{exp})$ and $\Delta H^{\text{at}}(\text{calc})$ must refer to the same phase. If the substance is solid or liquid, the phase transition enthalpy (sublimation or vaporization) has to be taken into account.

$$\Delta_f H^0(\text{g}) = \Delta_f H^0(\text{s}) + \Delta H^0(\text{phase transition}) \quad (5)$$

Consequently, the resonance energy will be:

$$E_{\text{resonance}} = \Delta H^{\text{at}}(\text{exp}) - \Delta H^{\text{at}}(\text{calc}) \quad (6)$$

All values are referred to the standard temperature (298.15 K).

The atomization energy of an amino-benzoic acid calculated from bond energies⁸ (eq. 4, see Table 5, for bond energy values) is 7750.8 kJ/mol if the specific value of the benzenoid carbon-carbon bond is taken

into account and 7522.8 kJ/mol, with single and double bond energies. The gas phase standard enthalpies of formation of the investigated compounds were calculated (eq. 5), by means of our experimental values of formation enthalpies in the solid state and of the sublimation enthalpies taken from the literature.¹¹

Table 5

The bond energies

Bond	C-H	C-C	C ^a -C ^a	C-N	N-H	C-O	C ^d -O ^d	O-H
Energy (kJ/mol)	412	348	518	305	388	360	743	463

The resulting resonance energies (eq. 6) are shown in Table 6. In the last column of this table the overall resonance energies of the isomeric amino-benzoic acids are shown, while the values of the precedent column exclude the resonance energy of the benzenoid ring. It may be seen that the lowest value of the atomization energy, and consequently of the resonance energy is met for the *meta* isomer, followed by *para* and *ortho*. The same order was reported by Nabavian *et al.*⁹, including for resonance energies calculated with the schemes of Klages and Franklin. This is the reversed order with respect to that observed in the crystalline state and this is due to very different values of the sublimation energies. In the crystalline state the *meta* isomer is building a zwitterion as was proved by Samsonowicz *et al.*¹², by means of quantum chemical computations and by means of IR and NMR spectra. In the gaseous state the structure of the *ortho* isomer is stabilized by the interaction between the neighbor carboxyl and the amino groups.

Table 6

Resonance energies of the isomeric amino-benzoic acids

Isomer amino-benzoic acid	$\Delta_{\text{subl}}H^0$ (kJ/mol)	$-\Delta H^{\text{at}}$ (exp) (kJ/mol)	E_{rez}^a (kJ/mol)	E_{rez}^b (kJ/mol)
<i>ortho</i>	104.9 ± 1.0	7805.3	54.5	282.5
<i>meta</i>	128.0 ± 3.2	7799.8	49.0	277.0
<i>para</i>	116.1 ± 3.7	7803.8	53.0	281.0

^a values of the resonance energies without the resonance energy of the benzenoid ring

^b overall resonance energies of the isomeric amino-benzoic acids

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