

The Enthalpies of Combustion and Formation of Nicotinic Acid and Creatinine

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The enthalpies of combustion of nicotinic acid and creatinine have been determined in an adiabatic rotating-bomb calorimeter. The enthalpies of formation have been obtained by combination of the experimental data with the accepted values for the enthalpies of formation of carbon dioxide and water. The results of other investigations on creatinine are discussed briefly. The resulting values and their estimated uncertainties are as follows:

	<i>Nicotinic acid</i>	<i>Creatinine</i>
$\Delta H_c^\circ(25^\circ\text{C})$	$-2730.67 \pm 0.57 \text{ kJ/mol}$	$-2334.53 \pm 0.86 \text{ kJ/mol}$
$\Delta H_f^\circ(25^\circ\text{C})$	$-344.97 \pm 0.62 \text{ kJ/mol}$	$-239.93 \pm 0.88 \text{ kJ/mol}$

Key words: Calorimetry; combustion; creatinine; enthalpy; formation; heat; nicotinic acid.

1. Introduction

This investigation is part of a program to obtain reliable thermodynamic data for important biochemical substances. Nicotinic acid and creatinine are compounds occurring in living processes and have biological as well as biochemical importance. Since nicotinic acid is used as a standard in clinical analyses there is need for reliable thermodynamic data which so far has been non-existent. There is also need for a standard reference material for use in the evaluation of calorimetric and analytical procedures involving nitrogen-containing compounds.

2. Materials

2.1. Benzoic Acid

The benzoic acid used for the calibration experiments and also as an auxiliary material was SRM calorimetric standard 39i obtained from the NBS Office of Standard Reference Materials. The purity of this material was given as 99.997 mole percent and the calorific value was certified to be 26434 J/g under certificate conditions. Conversion to thermodynamic standard state conditions gave $\Delta U_c^\circ(28^\circ\text{C})$ as -26410.36 J/g and $\Delta U_c^\circ(26^\circ\text{C})$ as -26412.35 J/g .

2.2. Creatinine

The sample of creatinine was obtained from the Office of Standard Reference Materials as SRM 914; it was certified as a chemical of known purity for use in the calibration and standardization of procedures

used in clinical analysis. The purity was certified to be 99.8 ± 0.1 percent. The impurities were given as: 0.03 percent volatile matter, 0.07 percent chloride, 0.003 percent ash, and 0.001 percent insoluble matter.

2.3. Nicotinic Acid

The nicotinic acid was obtained from the Office of Standard Reference Materials as SRM 148, a micro-analytical standard for use in checking determinations of carbon, hydrogen, and nitrogen. Although the absolute purity has not been established, the titrimetric assay indicates a purity of 99.99 ± 0.08 percent.

All samples were used as received with no attempts at further purification.

2.4. Oxygen

High-purity oxygen was used for both the benzoic acid calibration experiments and the nicotinic acid and creatinine combustion experiments. An analysis furnished with the cylinder showed the following impurities in ppm: Kr, 12.0; Xe, 0.7; N_2O , 0.8; N_2 , 3.0; and H_2O , 2.0. The presence of these impurities would have no significant effect on the values obtained for the combustion process.

3. Units and Conversion Factors

The 1969 Table of International Atomic Weights [1]¹ was used throughout this paper. The auxiliary data

¹Figures in brackets indicate the literature references at the end of the paper.

were taken from Selected Values of Chemical Thermodynamic Properties [2]. For conversion to joules from the conventional thermochemical calorie, one calorie was taken as equivalent to 4.1840 joules. All weighings were reduced to weights in vacuum by means of buoyancy corrections derived from air-density determinations.

4. Apparatus and Procedure

The adiabatic rotating-bomb calorimeter, the platinum lined bomb, the adiabatic temperature-control system, the ignition system and the temperature-measurement system have been described [3]. The volume of the empty bomb was 98 cm³.

The sample was pressed into a pellet and weighed into a platinum crucible using a micro-balance. The crucible, with the sample, was transferred to the crucible support of the bomb which was adjusted so that the sample was in contact with a 2 cm length of 0.075 mm diam platinum wire connected between the bomb electrodes. A small quantity of water (0.30 cm³ for the benzoic acid calibration experiments and 3.00 cm³ for the nicotinic acid and creatinine experiments) was added to the bomb which was then sealed, flushed with one liter of oxygen and filled with 31.62 atm of oxygen (1 atm = 101325 N/m²).

The bomb was placed in the calorimeter, the filling temperature was determined, the calorimeter jacket was evacuated and the adiabatic temperature controls placed in operation. The bomb was then heated electrically to 24.98 °C and the system left overnight for complete thermal equilibrium.

On the following morning temperatures were observed at intervals of a few minutes during a 30-minute initial rating period. The sample was then ignited by discharging a capacitor through the platinum fuse. Two minutes later the bomb was rotated to obtain a homogeneous solution; the rotation was not required for the benzoic acid calibration experiments because of the relatively small amount of nitric acid produced in the combustion. After about 15 minutes, thermal equilibrium was approached and calorimeter temperatures were determined at intervals of a few minutes during a final rating period. Because of the heating effort of the electric current through the platinum resistance thermometer there was a constant

increase of approximately 0.001 K per hour during the rating periods. The initial and final calorimeter temperatures were obtained by extrapolation of the time-temperature curves for the rating periods to the actual time of ignition.

It was not possible to ignite the creatinine with the platinum fuse; it was necessary to place a very small pellet of benzoic acid on top of the sample with the fuse in contact with the benzoic acid pellet. The fuse then ignited the pellet which in turn ignited the sample. This was not necessary with the nicotinic acid experiments.

The bomb was removed from the calorimeter, and the gaseous contents passed successively through a drying tube and a weighed CO₂-absorption tube. The bomb solution was removed, boiled to expel carbon dioxide, cooled and titrated with standard alkali, using a pH-meter, to determine the quantity of nitric acid produced in the combustion. No trace of nitrous acid was detected.

5. Results and Calculations

The results of the benzoic acid calibration experiments are given in tables 1 and 2 respectively. The calculations were performed by means of a computer program;² the values in the tables were taken and rounded from the print-out. The various items in the tables are described as:

EEE-std, the effective energy equivalent of the standard empty calorimeter including the bomb and all internal platinum parts except the crucible at the standard mean temperature of the experiment.

Cv-cont.(i), the heat capacity of all material added to the standard calorimeter, including crucible, sample, oxygen and water.

Corr to tm, a correction of 1.8 J/K to the heat capacity of the standard calorimeter for deviation of the actual mean temperature from the standard mean temperature.

Corr-parts, the calculated change in the heat capacity of the calorimeter due to alterations during the series.

²A computer program originally prepared by C. H. Shomate of the Naval Ordnance Test Station, China Lake, California, and later modified by G. T. Armstrong and E. J. Prosen, based upon the procedure of Hubbard, Scott, and Waddington [4].

TABLE 1. Results of the benzoic acid calibration experiments for a temperature rise of 1 °C.

Expt. No.	505	509	510	511	512	513
<i>EEE-std</i> , J/K	2518.26	2518.24	2517.80	2517.96	2518.19	2517.89
<i>Cv-cont</i> (i), J/K	4.54	4.54	4.54	4.55	4.55	4.52
<i>corr to std tm</i> , J/K	.09	.08	.10	.07	.01	.06
<i>corr-parts</i> , J/K	.00	.00	.00	.00	.00	.00
<i>EEE-actual</i> , J/K	2522.89	2522.86	2522.45	2522.57	2522.75	2522.47
Temp rise, K	1.083260	1.064585	1.072635	1.074361	1.014279	1.050943
<i>Q-total</i> , J	-2732.94	-2685.79	-2705.66	-2710.16	-2558.77	-2650.97
<i>q-ign</i> , J	1.08	1.24	1.04	1.08	1.16	1.19
<i>q-decomp</i> HNO ₃ , J	.09	.08	.08	.08	.12	.12
<i>q-WC</i> , J	2.01	1.97	1.99	2.00	1.89	1.94
<i>q-corr to std t_f</i> , J	-.01	-.01	-.01	-.01	.00	-.01
<i>Q-std react</i> , J	-2729.77	-2682.51	-2702.56	-2707.00	-2555.61	-2647.73
<i>m_s</i>	.103352	.101563	.102322	.102490	.096758	.100246
ΔU_c° (26 °C), J/g	-26412.35	-26412.35	-26412.35	-26412.35	-26412.35	-26412.35
Mean, <i>EEE-std</i> , J/K	2518.06					
sdm, J/K	0.08					

TABLE 2. Results of the benzoic acid calibration experiments for a temperature rise of 3 °C

Expt. No.	346	347	348	349	350	351	356	357
<i>EEE-std</i> , J/K	2519.04	2519.36	2518.64	2519.21	2518.53	2518.99	2518.62	2518.60
<i>Cv-cont</i> (i), J/K	4.79	4.72	4.74	4.75	4.76	4.75	4.75	4.75
<i>corr to std tm</i> , J/K	.41	.06	.13	.11	.16	.12	.13	.12
<i>corr-parts</i> , J/K	.02	.00	.00	.00	.00	.00	.00	.00
<i>EEE-actual</i> , J/K	2524.22	2524.15	2523.52	2524.08	2523.45	2523.86	2523.50	2523.47
Temp rise, K	3.482776	3.054576	3.135678	3.143009	3.166751	3.127852	3.142433	3.131127
<i>Q-total</i> , J	-8791.30	-7710.20	-7912.94	-7933.20	-7991.15	-7894.26	-7929.92	-7901.31
<i>q-ign</i> , J	.93	.86	.83	1.00	.90	.95	1.02	.85
<i>q-decomp</i> HNO ₃ , J	.14	.35	.51	.32	1.06	.63	.03	.03
<i>q-WC</i> , J	7.24	6.20	6.40	6.44	6.50	6.40	6.43	6.41
<i>q-aux</i> , J	.00	.00	.00	.00	.00	.00	.00	.00
<i>q-corr to std t_f</i> , J	-.18	-.02	-.05	-.05	-.06	-.04	-.05	-.05
<i>Q-react</i> , J	-8783.17	-7702.81	-7905.25	-7925.49	-7982.75	-7886.32	-7922.49	-7894.07
<i>m_s</i> , g	.332565	.291659	.299324	.300090	.302258	.298607	.299977	.298900
ΔU_c° (28 °C), J/g	-26410.36	-26410.36	-26410.36	-26410.36	-26410.36	-26410.36	-26410.36	-26410.36
Mean, <i>EEE-std</i> , J/K	2518.88							
sdm, J/K	0.112							

EEE-actual, the effective energy equivalent of the actual, fully loaded, calorimeter at the actual mean temperature of the experiment.

Temp. rise, the difference in K between the initial and final temperatures of the calorimeter obtained by extrapolation of the time-temperature curves to the time of ignition.

Q-total, the total energy absorbed by the calorimeter, obtained as the product of *EEE-actual* in J/K and the temperature rise in K.

q-ign, the quantity of electrical energy introduced into the calorimeter to ignite the sample.

q-decomp HNO₃, the theoretical quantity of energy required to decompose any nitric acid, formed in the combustion, into liquid water and gaseous nitrogen.

q-WC, the Washburn correction [4, 5] applied to convert the contents of the bomb in the initial and final states to their respective thermodynamic standard states.

q-aux, the standard heat of combustion of any auxiliary material, added to insure ignition or to enhance combustion, at the standard final temperature.

q-corr to std t_f, a correction to convert the energy evolved by the standard reaction at the actual final temperature to the selected standard final temperature.

Q-std reaction, the energy evolved by the standard reaction at the selected final temperature, obtained as the algebraic sum of *Q-total*, *q-ign*, *q-decomp HNO₃*, *q-WC*, *q-aux*, and *q-corr to std t_f*.

m_s, the weight of sample in vacuum.

ΔU_c° , the standard energy of combustion at constant volume at the selected final temperature, ob-

tained as *Q-std react./m_s*.

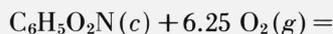
In the benzoic acid calibration experiments the values for *EEE-std* were calculated by iteration from ΔU_c° . Two series of calibration experiments were used for temperature rises of one and three degrees respectively.

The results of the experiments on nicotinic acid and on creatinine are given in tables 3 and 4, respectively.

The following values³ were used in the calculations:

	Density, g · cm ⁻³	C _p , J · g ⁻¹ · K ⁻¹	$\left(\frac{\partial U}{\partial P}\right)_T$, J · g ⁻¹ · atm ⁻¹
Benzoic acid ...	1.320	1.21	-0.013
Nicotinic acid...	1.47	1.19	- .007
Creatinine.....	1.31	1.23	- .005

The values obtained for nicotinic acid correspond to the process:



$$\Delta U_c^\circ (28^\circ\text{C}) = -22183.27 \pm 4.66 \text{ J/g}$$

$$\Delta U_c^\circ (28^\circ\text{C}) = -2731.02 \pm 0.57 \text{ kJ/mol}$$

$$\Delta H_c^\circ (28^\circ\text{C}) = -2730.39 \pm 0.57 \text{ kJ/mol}$$

$$\Delta H_c^\circ (25^\circ\text{C}) = -2730.67 \pm 0.57 \text{ kJ/mol}$$

$$\Delta H_f^\circ (25^\circ\text{C}) = -344.97 \pm 0.62 \text{ kJ/mol}$$

³The densities of nicotinic acid and creatinine were determined by a flotation procedure; the heat capacities and compressibility coefficient of nicotinic acid and creatinine were estimated.

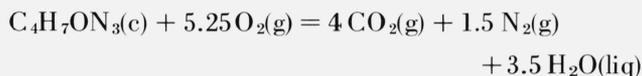
TABLE 3. Results of the calorimetric combustion experiments on nicotinic acid

Expt. No.	352	353	354	355	358	359
<i>EEE-std</i> , J/K	2518.88	2518.88	2518.88	2518.88	2518.88	2518.88
<i>Cv-cont(i)</i> , J/K	15.94	16.03	16.01	16.02	16.02	4.82
<i>corr to tm</i> , J/K	-.49	.10	-.05	.05	.05	-.36
<i>corr parts</i> , J/K	.00	.00	.00	.00	.00	.00
<i>EEE-actual</i> , J/K	2534.33	2535.01	2534.84	2534.94	2534.95	2523.34
Temp rise, K	2.467210	3.128016	2.950755	3.058636	3.076341	2.635465
<i>Q-total</i> , J	-6252.72	-7929.54	-7479.69	-7753.46	-7798.36	-6650.17
<i>q-ign</i> , J	.97	.83	.95	.71	.99	.81
<i>q-decomp HNO₃</i> , J	15.54	19.58	18.13	19.68	19.40	16.52
<i>q-WC</i> , J	9.24	11.89	11.18	11.59	11.67	5.90
<i>q-aux</i> , J	.00	.00	.00	.00	.00	.00
<i>q-corr to std t_f</i> , J	0.11	-.03	.01	-.02	-.02	.08
<i>Q-std react</i> , J	-6226.86	-7897.27	-7449.42	-7721.50	-7766.32	-6626.85
<i>m_s</i>	.280691	.356061	.335815	.348040	.350096	.298723
$\Delta U_c^\circ (28^\circ\text{C})$, J/g	-22184.02	-22179.53	-22183.08	-22185.66	-22183.39	-22183.93
Mean $\Delta U_c^\circ (28^\circ\text{C})$, J/g	-22183.27					
sdm, J/g	±0.83					

TABLE 4. Results of the calorimetric combustion experiments on creatinine.

Expt. No.	500	501	502	503	504	506
EEE-std, J/K	2518.06	2518.06	2518.06	2518.06	2518.06	
Cv-cont(i), J/K	15.73	15.73	15.73	15.73	15.74	15.76
corr to tm, J/K	.10	.09	.13	.09	.24	.07
corr parts, J/K	-.01	-.01	-.01	-.01	-.01	-.01
EEE-actual, J/K	2533.89	2533.87	2533.92	2533.87	2534.06	2533.89
Temp rise, K	1.112177	1.097550	1.136384	1.097280	1.264700	1.077063
Q-total, J	-2818.14	-2781.05	-2789.50	-2780.37	-3204.80	-2729.16
q-ign, J	1.22	.89	1.01	1.16	1.01	1.08
q-decomp HNO ₃ , J	11.78	11.85	12.27	11.60	13.92	10.13
q-WC, J	3.29	3.25	3.38	3.27	3.77	3.21
q-aux, J	240.91	253.65	339.90	370.11	439.81	200.86
q-corr to t _f , J	-.02	-.02	-.02	-.02	-.05	-.01
Q-std react, J	-2560.96	-2511.43	-2522.98	-2394.25	-2746.34	-2513.89
m _s , g	.124008	.121736	.122270	.115978	.133045	.121746
ΔU _c ^o (26 °C), J/g	-20651.53	-20630.07	-20634.56	-20644.07	-20642.14	-20648.70
Mean, ΔU _c ^o (26 °C), J/g	-20641.84					
sdm, J/g	±3.35					

The values obtained for creatinine correspond to the process:



$$\Delta U_c^\circ (26^\circ\text{C}) = -20641.84 \pm 7.64 \text{ J/g}$$

$$\Delta U_c^\circ (26^\circ\text{C}) = -2334.99 \pm .86 \text{ kJ/mol}$$

$$\Delta H_c^\circ (26^\circ\text{C}) = -2334.37 \pm .86 \text{ kJ/mol}$$

$$\Delta H_c^\circ (25^\circ\text{C}) = -2334.53 \pm .86 \text{ kJ/mol}$$

$$\Delta H_f^\circ (25^\circ\text{C}) = -239.93 \pm .88 \text{ kJ/mol}$$

The uncertainties assigned to ΔU_c° and ΔH_c° were obtained by combining 2 sdm for the calibration experiments with 2 sdm for the combustion experiments, 0.01 percent for the uncertainty in the certified value for benzoic acid, 0.01 percent for systematic errors and 0.01 percent for the possible effects of impurities in the sample. The uncertainty assigned to ΔH_f° was obtained by combination of the uncertainty in ΔH_c° with 0.01 percent in the values taken for the heats of formation of carbon dioxide and water.

The results of the carbon dioxide analyses are given in table 5; the values given were obtained by

$$\frac{\text{CO}_2(\text{actual}) - \text{CO}_2(\text{theor. for auxiliary})}{\text{CO}_2(\text{theor. for sample})}$$

TABLE 5. Results of the CO₂ analyses

Expt. No.	Nicotinic acid	Expt. No.	Creatinine
352	0.9989	500	0.9950
353	.9988	501	.9954
354	.9984	502	.9978
355	.9981	503	.9980
358	.9993	504	.9983
359	.9995	506	.9972
avg	.9988	avg	.9970

The preliminary work on creatinine showed that when larger samples were used (sufficient to obtain a 3-degree temperature rise) there was evidence of incomplete combustion. Reduction of the amount of sample significantly improved the stoichiometry

of the combustion process; the relative amount of benzoic acid used (an auxiliary for ignition) had little or no effect on the stoichiometry.

6. Comparison With Existing Data

Two prior determinations of the enthalpy of combustion of creatinine have been reported. Emery and Benedict [6] obtained the enthalpy of combustion based upon the quantity of carbon dioxide produced in the reaction. Their data was recalculated on the basis of sample weight by Huffman, Ellis, and Fox [7], who also made an independent determination of the enthalpy of combustion. We have corrected these values for changes in atomic weights and have obtained the following values:

$$\Delta H_c^\circ \text{ kJ/mol}$$

$$-2328.8 \pm 5.4 \quad \text{Emery and Benedict [5]}$$

$$-2335.97 \pm 0.67 \quad \text{Huffman, Ellis, and Fox [6]}$$

$$-2334.53 \pm 0.88 \quad \text{This investigation}$$

Huffman, Ellis, and Fox used a paper and platinum wire technique to ignite the sample. They found the samples to be somewhat hygroscopic which may have been due to an electrostatic charge on the pellet.

No previous determinations have been reported on the enthalpy of combustion of nicotinic acid.

7. References

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