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Enthalpies of Combustion of Organic Compounds. IV. Acetanilide and Nicotinic Acid**

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Standard energies of combustion at 298.15 K have been determined for crystalline acetanilide and nicotinic acid by static oxygen bomb calorimetry. Derived standard enthalpies of combustion and of formation are $-(4224.8\pm1.0)$ and $-(209.5\pm1.5)$ kJ mol^{-1} for acetanilide, and $-(2730.83\pm0.48)$ and $-(344.81\pm0.92)$ kJ mol^{-1} for nicotinic acid, respectively. Nicotinic acid pellets of 1.2 g in mass showed remarkable tendency to spatter when partially burnt. Factors governing the completeness of combustion of the material have been explored through 28 test combustion experiments.

The role and desired properties of test substances in combustion calorimetry were discussed in detail by Armstrong and Johnson[1] and by Cox.[2] A recommendation was issued from IUPAC on reference materials for enthalpy measurements including combustion calorimetry.[3] Urea,[1-3] acetanilide,[2-4] hippuric acid,[3] and tris(hydroxymethyl)aminomethane[3] were recommended or proposed as test substances and nicotinic acid[1] as a candidate, for oxygen bomb combustion calorimetry of organic compounds containing carbon, hydrogen, oxygen and nitrogen.

For acetanilide and nicotinic acid, Johnson determined standard enthalpies of combustion.[1,4,5] Johnson's value for acetanilide[4] is in good agreement with the value deduced from Wadsö's reaction calorimetric results.[6] However, no other combustion calorimetric results have been reported so far for these compounds.

In this paper, results of combustion calorimetric studies on these compounds are reported. In the course of this study, remarkable tendency of spattering during burning was found for nicotinic acid, so twenty-eight test combustion experiments were carried out on this compound in order to disclose requirements to realize complete combustion. The results of these test experiments are also reported.

Experimental

Materials. Acetanilide used in this study was a commercial standard material for organic microanalysis (Kishida, SMA-SP-1) prepared under the certification of a subcommission of the Japan Society for Analytical Chemistry. The sample as received was pressed into pellets and used in the experiments. The purity was found to be higher than 99.9 mole per cent by the analysis of DSC heating curves in the melting region. Nicotinic acid was a commercial reagent (Nakarai, G. R.), which was purified by recrystallization from aqueous solution and then from ethanol solution, followed by fractional sublimation *in vacuo* and recrystallization from aqueous solution. The last-mentioned step was additionally carried out, since DSC heating curves in the melting region for the sublimed sample gave an indication that it was in a metastable crystalline state. The recrystallized sample was dried *in vacuo* (about 1 Pa) and then subjected to pellet-drying[7-9] to remove a trace of occluded water. Pellets were produced again and stored on anhydrous magnesium perchlorate for one week. The purity of the purified nicotinic acid was found to be higher than 99.9 mole per cent by the method mentioned above. In the test combustion experiments on nicotinic acid, the untreated reagent as well as the purified material was employed. No significant difference was observed between these samples in the tendency of spattering.

Combustion Calorimetry. A constant temperature jacket type rotating bomb calorimeter with a platinum-lined bomb, described elsewhere,[10,11] was used without rotating the bomb. The samples were burnt at 3.04 MPa of oxygen pressure in the presence of 1 g of water. An ordinary platinum crucible with no lid(denoted by **a**; Parr, 43A5, 2.4 cm in diameter, 1.2 cm in depth, and 11 g in mass) was used for acetanilide. For nicotinic acid, a platinum crucible with a small lid[12] (denoted by **b**; 2.4 cm in diameter, 2.5 cm in depth, and 29.5 g in mass) was used to prevent the incomplete combustion. The calorimeter was calibrated by burning thermochemical standard benzoic acid (U.S. National Bureau of Standards, SRM 39i) under certificate conditions. Mean and standard deviation of the mean for the energy equivalent of the empty calorimetric system were (15158.53 ± 0.58) and (15166.91 ± 0.33) J K^{-1} for acetanilide and nicotinic acid experiments, respectively.

Nitric acid was determined by titration with aqueous sodium hydroxide. Carbon monoxide was barely detected in the present combustion calorimetric experiments.

Relative atomic masses were taken from the recommendation of IUPAC Commission on Atomic Weights (1977). Densities, specific heat capacities, and $(\partial U/\partial p)_T$ values at 298.15 K were taken from Refs. 4 and 5. Specific standard enthalpy of combustion at 298.15 K for cotton fuse ($CH_{1.86}O_{0.93}$) was -16507 J g^{-1} and the internal volume of the bomb was 0.3458 dm^3. Uncertainties in this paper are uncertainty intervals defined by Rossini,[13] unless otherwise stated.

Test Combustion Experiments on Nicotinic Acid. Measured amounts of nicotinic acid were pressed into pellets and they were ignited in the same way as in the combustion calorimetric experiments. After every test experiment, the internal surface and the internal fittings of the bomb were visually examined.

Results and Discussion

Combustion Tests on Nicotinic Acid. As was mentioned above briefly, nicotinic acid showed remarkable tendency of spattering to cause incomplete combustion,

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TABLE 1. SUMMARY OF RESULTS OF TEST COMBUSTION ON NICOTINIC ACID

Series	$\frac{m(\text{sample})}{\text{g}}$	Pellet preparation method[a)]	Crucible[b)]	Number of experiments in which combustion was:	
				Complete	Incomplete
I	1.2	A	**a**	1	7
II	1.2	B	**a**	3	3
III	1.2	A	**b**	8	1
IV	0.3	A	**a**	0	2
V	0.3	B	**a**	0	3

a) A: The use of a hand pellet press, B: the use of a high pressure and an evacuable die. b) **a**: An ordinary platinum crucible with no lid, **b**: a deep platinum crucible with a small lid.

when a sample pellet weighing 1.2 g was ignited in an open crucible at 3 MPa of oxygen pressure. Nicotinic acid of 1.2 g mass gives rise to an adiabatic temperature rise of about 1.8 K for our calorimeter, which is of similar magnitude to that for the calibration experiments. In order to evaluate the degree of difficulty of combustion of this material, twenty-eight test combustion experiments were undertaken. If combustion is complete, carbon dioxide, water, nitrogen, and a small amount of nitric acid alone will be produced. The presence of the unburnt material, the carbonized material, or soot, in the bomb after the combustion, is taken to be the evidence of incomplete combustion in this context.

Two methods of pellet preparation were tested. One is the use of a commercial hand pellet press (Parr, 2811), which has been used in most of combustion calorimetric works in this laboratory(method A). The other is the use of a high pressure press with an evacuable die, which has been used for preparing KBr discs for infrared spectrometry (method B). The die, which was charged with powdered nicotinic acid, was evacuated, and then the powder was pressed at 700 MPa to produce a pellet. The die for method A cannot be evacuated. Two kinds of crucibles were examined: crucibles **a** and **b**, described in the experimental section. Pellets of two masses were tested: 1.2 and 0.3 g. Results of the test combustion experiments are given in Table 1.

In series I, pellets weighing 1.2 g were prepared by method A and ignited in crucible **a**. Combustion was complete in one of eight experiments. In the other seven experiments, unburnt nicotinic acid lumps, covered with the carbonized material, were found spattered on the internal bomb wall. This suggests that the fragmentation of the pellets occured in the course of combustion, and the extinction of fire resulted by the collision of the burning fragments with the cold bomb wall.

In series II, pellets weighing 1.2 g were produced by method B, and ignited in crucible **a**. Of six experiments, combustion was complete in three. In the other experiments, the deposition of a small amount of soot was observed on the internal bomb wall, but the spattering of unburnt sample was not experienced. The adoption of the high pressure and the evacuation of the die, both of which would serve to prepare rigid pellets, were considerably effective in suppressing the fragmentation. However, the method used in this series was not sufficient to produce complete combustion.

In series III, pellets weighing 1.2 g were prepared by method A and ignited in crucible **b**. Although spattering was observed in one of nine experiments, combustion was complete in the other eight experiments. The small lid would act as baffle for spattering fragments and at the same time it would serve to form a hot zone in the crucible to prevent the soot formation. This series was the most successful one and the method of this series was adopted in the combustion calorimetric experiments, as described in the experimental section.

In Johnson's experiments,[2)] in which pellets weighing 0.3 g were ignited in a crucible with no baffle plate at 3 MPa of oxygen pressure, incomplete combustion was not experienced.[16)] In order to study the effect of mass decrease on the completeness of combustion, experiments of series IV and V were conducted. Pellets weighing 0.3 g were produced by method A(series IV) or B(series V) and ignited in crucible **a**. In series IV, a small amount of soot was found only in the crucible. In these series, spattering was not experienced. Thus, the decrease of mass was confirmed to be effective in preventing the spattering. The soot formation in these series would probably be caused by insufficient temperature rise around the crucible during combustion, owing to the decrease of mass of the material.

To summarize, the methods other than the use of a crucible with a small lid are more or less insufficient to get complete combustion of a nicotinic acid pellet of the present size. This is the conclusion of the present study on the difficulty of complete combustion of nicotinic acid. The characteristics, disclosed in this study, should be taken into consideration properly, when the material is scrutinized as a candidate test substance.

Standard Enthalpies of Combustion. Each of six combustion calorimetric experiments was carried out for both compounds. Standard energies and enthalpies of combustion reported in this paper refer to the following idealized combustion reactions at 298.15 K:

$$C_aH_bO_cN_d(c) + [(4a+b-2c)/4]O_2(g) = aCO_2(g) + (b/2)H_2O(l) + (d/2)N_2(g), \quad (1)$$

where $a=8$, $b=9$, $c=1$, and $d=1$ for acetanilide and

Table 2. Summary of combustion calorimetric results on acetanilide

Experiment	1	2	3	4	5	6
m'(compd)/g	0.86912	0.86603	0.86086	0.86390	0.86756	0.86490
m'''(fuse)/g	0.00256	0.00308	0.00290	0.00298	0.00278	0.00285
$m^{i}(H_2O)$/g	1.172	1.112	1.219	1.155	1.216	1.188
p^{i}(gas)/MPa	3.040	3.040	3.043	3.043	3.079	3.047
$(T_i-273.15\ K)$/K	23.20757	23.21368	23.19775	23.18550	23.16898	23.17702
$(T_f-273.15\ K)$/K	25.03053	25.02821	25.00493	25.00034	24.98584	24.98874
ΔT_{corr}/K	0.02690	0.02693	0.02849	0.02874	0.02509	0.02446
ΔU_{ign}/J	5.4	5.4	7.1	7.1	5.8	6.0
ΔU_{Σ}/J	14.7	14.4	14.7	14.6	14.9	14.7
$\Delta U_d(HNO_3)$/J	47.5	14.9	47.2	46.1	46.3	45.2
ε^{i}(cont)/J K^{-1}	17.9	20.3	18.1	17.8	24.4	24.2
ε^{f}(cont)/J K^{-1}	19.1	21.6	19.3	19.0	25.6	25.4
$-\Delta U_{IBP}$/J	27252.3	27128.3	26987.8	27099.7	27198.1	27129.2
$-\{\Delta U_c^{\circ}/M\}$/kJ g^{-1}	31.2359	31.2324	31.2223	31.2417	31.2267	31.2431
$-\Delta U_c^{\circ}$/kJ mol^{-1}	4222.01	4221.54	4220.17	4222.80	4220.76	4222.98

Table 3. Summary of combustion calorimetric results on nicotinic acid

Experiment	1	2	3	4	5	6
m'(compd)/g	1.18214	1.24063	1.23510	1.24509	1.24186	1.24401
m'''(fuse)/g	0.00296	0.00290	0.00276	0.00266	0.00260	0.00288
$m^{i}(H_2O)$/g	1.123	1.193	1.123	1.178	1.114	1.137
p^{i}(gas)/MPa	3.049	3.038	3.055	3.076	3.053	3.033
$(T_i-273.15\ K)$/K	23.23376	23.14182	23.15302	23.13627	23.13809	23.14096
$(T_f-273.15\ K)$/K	24.99437	24.99146	24.99010	24.98798	24.98567	24.99136
ΔT_{corr}/K	0.02805	0.03037	0.02634	0.02619	0.02710	0.02717
ΔU_{ign}/J	4.3	4.9	6.1	6.1	2.4	6.1
ΔU_{Σ}/J	20.4	21.6	21.5	21.9	21.6	21.5
$\Delta U_d(HNO_3)$/J	26.7	27.7	29.5	28.0	24.7	22.0
ε^{i}(cont)/J K^{-1}	20.6	20.9	20.7	21.0	20.6	20.7
ε^{f}(cont)/J K^{-1}	21.6	21.9	21.7	22.0	21.7	21.7
$-\Delta U_{IBP}$/J	26308.8	27625.8	27494.8	27720.1	27645.9	27684.1
$-\{\Delta U_c^{\circ}/M\}$/kJ g^{-1}	22.1910	22.1893	22.1830	22.1883	22.1899	22.1808
$-\Delta U_c^{\circ}$/kJ mol^{-1}	2731.93	2731.73	2730.95	2731.60	2731.80	2730.67

a=6, b=5, c=2, and d=1 for nicotinic acid. Combustion calorimetric results on these compounds are presented in Tables 2 and 3. Symbols in these tables are essentially similar to those used by Hubbard *et al.*[14] except for ΔU_{Σ}, the sum of contributions from items 81—85, 87—91, and 93—94 as defined by Hubbard *et al.*[14] Mean and standard deviation of mean of the standard energies of combustion, $\{\Delta U_c^{\circ}/M\}$, are $-(31.2337\pm0.0037)$ and $-(22.1821\pm0.0017)$ kJ g^{-1} for acetanilide and nicotinic acid, respectively.

Derived molar standard thermodynamic quantities are presented and compared with literature values in Table 4. The following CODATA key values for thermodynamics[15] were used to calculate standard enthalpies of formation of both compounds: $\Delta H_f^{\circ}(CO_2, g) = -(393.51 \pm 0.13)$ and $\Delta H_f^{\circ}(H_2O, l) = -(285.830\pm0.042)$ kJ mol^{-1}, where uncertainties are those at the 95 per cent confidence level.

Uncertainties attached to the values of ΔU_c°(c) and ΔH_f°(c) are the uncertainty intervals, defined by Rossini.[13] Uncertainties for the values of ΔH_f°(c) are the square roots of the sum of the squares of weighted uncertainties of ΔH_f°(c), $\Delta H_f^{\circ}(CO_2, g)$, and $\Delta H_f^{\circ}(H_2O, l)$. The weight for ΔH_f°(c) is 1, and those for $\Delta H_f^{\circ}(CO_2, g)$ and $\Delta H_f^{\circ}(H_2O, l)$ are a and $(b/2)$, given in Eq. 1, respectively. Uncertainties of Johnson's standard enthalpies of combustion and of formation[4,5] were recalculated so as to be in accord with the present assignment. The standard enthalpy of formation from Wadsö's experiments on acetanilide was quoted from Ref. 2.

Table 4. Standard thermodynamic quantities at 298.15 K of acetanilide and nicotinic acid and comparison with literature values

	$-\Delta U_c^{\circ}$(c) / kJ mol^{-1}	$-\Delta H_c^{\circ}$(c) / kJ mol^{-1}	$-\Delta H_f^{\circ}$(c) / kJ mol^{-1}
Acetanilide			
Johnson[4]	4221.78±0.75	4224.88±0.75	209.4 ±1.3
Wadsö[6]	——	——	209.37±0.69
This work	4221.7 ±1.0	4224.8 ±1.0	209.5 ±1.5
Nicotinic acid			
Johnson[5]	2731.29±0.38	2730.67±0.38	344.97±0.87
This work	2731.45±0.48	2730.83±0.48	344.81±0.92

The standard enthalpies of combustion for both compounds, obtained in this study, agree with those of Johnson[4,5] within the assigned uncertainties. The present standard enthalpy of formation for acetanilide is in agreement with Wadsö's reaction calorimetric value[6] within the assigned uncertainties. Thus, standard enthalpies of combustion for these compounds have been determined more confirmatively.

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