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Enthalpies of Combustion of Organic Compouds. V. 3- and 4-Nitroanilines[†]

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Synopsis. Precision oxygen bomb combustion calorimetry was carried out for the title compounds in the crystalline states. Standard enthalpies of formation at 298.15 K for the crystalline and gaseous states were derived.

Although standard enthalpies of combustion has been reported for 3- and 4-nitroanilines by several authors,[1–4] the agreement between these values is poor. In order to obtain more reliable values, oxygen bomb combustion calorimetry accompanying carbon dioxide analysis has been conducted for these compounds.

Experimental

Materials. Microanalytical standard 4-nitroaniline (Kishida, SMA-SP-18) was used after applying the pellet drying procedure.[5] Commercial 3-nitroaniline (Wako, special Grade) was purified by recrystallization from aqueous solution and then from ethanol solutions (three times). After preliminary drying, the purified material was subjected to the pellet drying.

Combustion Calorimetry. An isoperibol rotating bomb calorimeter, described elsewhere,[6,7] was used without rotating the bomb. The calorimeter was calibrated by burning thermochemical standard benzoic acid (N. B. S. SRM 39i) under certificate conditions. Mean and standard deviation of the mean for the energy equivalent of the empty calorimeter, ε°(calor), was obtained to be (15 163.52±0.51) J K^{-1} from eight calibration experiments. The substances were found to produce a small amount of soot, when a pellet weighing about 1.2 g was ignited alone in an ordinary open crucible at 3 MPa of oxygen pressure. The use of a deep crucible with a small lid[8] or the use of a higher pressure (4 MPa) was not efficient in preventing the soot formation. Consequently, a pellet of the thermochemical standard benzoic acid, weighing 0.3 g, was placed on a pellet of either substance in the ordinary crucible, and they were ignited at 3 MPa of oxygen pressure. In this way, the soot formation was effectively suppressed. In order to examine the completeness of combustion and/or the purity of tha sample, carbon dioxide recovery was determined by the method described previously.[7] Carbon monoxide was barely detected. Nitric acid was determined by titration with aqueous sodium hydroxide solution.

Table 1. Auxiliary data for the calculation of standard energy of combustion

Material	Formula	ρ / g cm^{-3}	c_p / J K^{-1} g^{-1}	$-(\partial U/\partial p)_T$ / J MPa^{-1} g^{-1}
3-Nitroaniline	$C_6H_6O_2N_2$	1.430	1.15	(0.048)
4-Nitroaniline	$C_6H_6O_2N_2$	1.424	1.116	(0.048)
Benzoic acid	$C_7H_6O_2$	1.320	1.21	0.0527
Cotton fuse	$CH_{1.86}O_{0.93}$	1.5	1.7	0.0290

Auxiliary Quantities. 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 are collected in Table 1. Other auxiliary quantities are as follows: T_h=298.15 K, V(bomb)=0.3469 cm^3, ΔU_c°(fuse)=−16507 J g^{-1}, and $\Delta U_c^\circ/M$(benzoic acid)=−(26414±1) J g^{-1}, where uncertainty is the estimated standard deviation of the mean.

Results

Molar srandard energies and enthalpies of combustion, given in this paper, refer to the following idealized combustion reaction at 298.15 K: $C_6H_6O_2N_2(c)+(13/2)O_2(g)=6CO_2(g)+N_2(g)+3H_2O(l)$. Details of the combustion calorimetry are presented in Table 2. Most of the symbols in the table are essentially similar to those used by Hubbard *et al.*[9] Mean and standard deviation of the mean for molar standard energy of combustion, ΔU_c°(c), and those for relative total carbon dioxide recovery, [m(CO$_2$,obsd)/m(CO$_2$,calcd)], are

Table 2. Summary of combustion calorimetric results on 3- and 4-nitroanilines

Experiment	3-Nitoaniline				4-Nitroaniline				
	1	2	3	4	1	2	3	4	5
m'(compd)/g	0.85161	0.84414	0.84702	0.84879	0.84963	0.84914	0.84788	0.85055	0.85704
m''(B-acid)/g	0.30065	0.29354	0.30007	0.29804	0.30266	0.29427	0.29286	0.30742	0.30647
m'''(fuse)/g	0.00234	0.00257	0.00270	0.00220	0.00191	0.00230	0.00236	0.00205	0.00273
m^i(H$_2$O)/g	3.14	3.17	3.05	3.15	3.07	3.17	3.13	3.07	3.00
$(T_i$/K)−273.15	23.14719	23.14226	23.14067	23.14000	23.13275	23.13830	23.14895	23.12804	23.12626
$(T_f$/K)−273.15	24.99401	24.97222	24.98451	24.98326	24.97713	24.97061	24.97411	24.97976	24.98690
ΔT_{corr}/K	0.02699	0.02882	0.02700	0.02743	0.02357	0.02719	0.02434	0.02167	0.02135
n^f(HNO$_3$)/mmol	1.152	1.160	1.167	1.167	1.142	1.129	1.192	1.154	1.154
ΔU_{ign}/J	7.7	7.7	7.8	7.8	7.8	7.8	2.5	7.5	7.6
ΔU_Σ/J	22.1	21.8	21.8	22.0	22.0	21.9	21.7	22.0	22.0
ΔU_d(HNO$_3$)/J	67.8	68.3	68.7	68.7	67.2	66.5	70.2	68.0	68.0
ε^i(cont)/J K^{-1}	26.3	26.4	25.9	26.3	26.0	26.4	26.2	24.0	23.7
ε^f(cont)/J K^{-1}	27.3	27.4	26.9	27.3	27.0	27.4	27.2	25.0	24.7
$-\Delta U_{IBP}$/J	27717.0	27351.6	27590.9	27575.8	27649.4	27411.5	27351.1	27784.3	27923.7
$-\{\Delta U_c^\circ/M$(compd)}/kJ g^{-1}	23.0706	23.0597	23.0571	23.0640	22.9916	22.9791	22.9805	22.9739	22.9787
$-\Delta U_c^\circ$(compd)/kJ mol^{-1}	3186.63	3185.13	3184.77	3185.72	3175.72	3173.98	3174.19	3173.26	3173.93
[m(CO$_2$, obsd)/m(CO$_2$, calcd)]	1.0000	1.0001	—	1.0005	1.0002	1.0001	1.0005	0.9995	0.9997

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Table 3. Standard thermodynamic quantities at 298.15 K of 3- and 4-nitroanilines

	3-Nitroaniline	4-Nitroaniline
$-\Delta U_c^\circ(c)$/kJ mol^{-1}	3185.56 ± 0.88	3174.22 ± 0.90
$-\Delta H_c^\circ(c)$/kJ mol^{-1}	3184.32 ± 0.88	3172.98 ± 0.90
$-\Delta H_f^\circ(c)$/kJ mol^{-1}	34.2 ± 1.2	45.6 ± 1.2
ΔH_{sub}°/kJ mol^{-1}	96.7 ± 1.3[a]	100.8 ± 1.3
$\Delta H_f^\circ(g)$/kJ mol^{-1}	62.5 ± 1.8	55.2 ± 1.8

a) Ref. 11.

Table 4. Comparison of the present results with literature values

	$-\Delta H_c^\circ(c)$/kJ mol^{-1}
3-Nitroaniline	
Médard and Thomas(1957)[a]	3190.3 ± 6.3
Lebedeva *et al.* (1971)[b]	3180.3 ± 0.4
Present study	3184.32 ± 0.88
4-Nitroaniline	
Cole and Gilbert (1951)[c]	3177.08 ± 0.63
Médard and Thomas(1954)[d]	3180.1 ± 3.2
Lebedeva *et al.* (1971)[b]	3175.7 ± 0.8
Present study	3172.98 ± 0.98

a) Ref. 2. b) Ref. 3. c) Ref. 1. d) Ref. 4.

$-(3185.56\pm0.41)$ kJ mol^{-1} and (1.0002 ± 0.0001), respectively, for 3-nitroaniline, and $-(3174.22\pm0.41)$ kJ mol^{-1} and (1.0002 ± 0.0001), respectively, for 4-nitroaniline.

Derived standard thermodynamic quantities are presented in Table 3. CODATA key values of thermodynamics[10] and the calorimetric values of standard enthalpy of sublimation, reported by Malaspina *et al.*,[11] were used to calculate $\Delta H_f^\circ(c)$ and $\Delta H_f^\circ(g)$, respectively. Uncertainties for $\Delta U_c^\circ(c)$ and $\Delta H_c^\circ(c)$ are the uncertainty intervals defined by Rossini.[12] Those for $\Delta H_f^\circ(c)$ and $\Delta H_f^\circ(g)$ were calculated by combining the relevant uncertainties by use of the equation of error propagation.

Discussion

The present values are compared with literature values in Tabel 4. The present value for 3-nitroaniline is intermediate between the literature values. The one for 4-nitroaniline is less negative than the rest. Although the present value is closer to that of Levedeva *et al.*,[3] they do not agree with each other within the sum of the uncertainties. The present results for both substances, seem to be more reliable, since the chemical aspect of the combustion calorimetry is evidenced to be quite normal by the results of carbon dioxide analysis.

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