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Standard Enthalpies of Combustion and Vaporization of *N*,*N*-Dimethylaniline[**]

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Synopsis. Standard energy of combustion and standard enthalpy of vaporization of *N*,*N*-dimethylaniline have been determined by oxygen bomb combustion calorimetry and vaporization calorimetry, respectively. Derived standard enthalpies at 298.15 K are as follows: $\Delta H_c^\circ(1) = -(4767.8 \pm 3.2)$, $\Delta H_f^\circ(1) = (47.7 \pm 3.4)$, $\Delta H_v^\circ = (52.83 \pm 0.03)$, and $\Delta H_f^\circ(g) = (100.5 \pm 3.4)$ kJ mol^{-1}, respectively.

Despite the fact that *N*,*N*-dimethylaniline is one of the representative tertiary amines, literature data of standard thermodynamic quantities are meager. We have determined standard energy of combustion and standard enthalpy of vaporization, both at 298.15 K, by calorimetric methods. Results of these measurements are briefly reported in this note.

Experimental

Materials. Commercial *N*,*N*-dimethylaniline (Wako, Special Grade) was purified by treatment with acetic anhydride, hydrochloric acid, tin(II) chloride, and aqueous sodium hydroxide, followed by extraction with diethyl ether, drying with sodium hydroxide, fractional distillation at reduced pressure (twice) and drying with calcium hydride. Gas-liquid chromatographic analysis using PEG 20M as liquid phase gave the purity of 99.96 mass per cent.

Combustion Calorimetry. An isoperibol rotating bomb calorimeter with a platinum-lined bomb of Osaka University, described elsewhere,[1,2] was used without rotating the bomb. The calorimeter was calibrated by burnig thermochemical standard benzoic acid (U. S. National Bureau of Standards, SRM 39i) under certificate conditions. Mean and standard deviation of the mean (sdm) for the energy equivalent of the empty calorimetric system ε(calor)[5] was determined to be (15161.67±0.74) J K^{-1} from eleven calibration experiments.

N,*N*-Dimethylaniline, which had been placed in a glass vacuum system together with activated molecular sieve 4A, was transfered into a vessel, where inverted soft glass ampoules with a thin tubular stem had been located, by vacuum distillation, and then charged into the ampoules under the pressure of dry nitrogen. The fine neck of the ampoule was fused at the outside of the vacuum system with a small city-gas flame to seal the ampoule. The ampoule filled with a sample was placed in an open platinum crucible together with a small amount of paraffin oil which acted as a promoter, and combustion was started by igniting the oil at 3 MPa of oxygen pressure.

Complete combustion was achieved by reducing the mass of *N*,*N*-dimethylaniline to below 0.26 g, while adjusting the mass of the paraffin oil so that the resultant corrected temperature rise would be similar to that of the calibration experiments (1.84 K). Otherwise, the formation of soot in the crucibles or the formation of yellow colored bomb solution with irritating odor resulted. Only four experiments were successful.

Vaporization Calorimetry. A carrier-gas type vaporization calorimeter of Miyazaki University[3] was used. The calorimetric system was tested by measuring ΔH_v° of cyclohexane and decane. Mean and sdm of each of five determinations were (33.03±0.04) and (51.36±0.06) kJ mol^{-1} for cyclohexane and normal decane, respectively, while the recommended values[4] are (33.03±0.04) and (51.35±0.04) kJ mol^{-1}, respectively.

Auxiliary Quantities. Relative atomic masses were taken from the recommendation of the IUPAC Commission on Atomic Weights (1977). Densities, specific heat capacities, $(\partial U/\partial p)_T$ values, and specific energies of combustion of the paraffin oil and cotton fuse, are collected in Table 1. Internal volume of the bomb was 0.3469 dm^3.

Results and Discussion

Results of combustion calorimetric experiments on *N*,*N*-dimethylaniline are presented in Table 2. Molar standard energy of combustion given in this table refer to the following idealized combustion reaction at 298.15 K: $C_8H_{11}N(1) + (43/4)O_2(g) = 8CO_2(g) + (11/2) \cdot H_2O(1) + (1/2)N_2(g)$. Most of the symbols used in Table 2 are essentially similar to those used by Hubbard *et al.*[5] ΔU_Σ denotes the sum of contributions from items 81—85 and 87—94 as defined in Ref. 5. The mean and sdm of observed molar standard energies of combustion were $-(4762.2 \pm 1.3)$ kJ mol^{-1}.

Results of vaporization calorimetric experiments are summarized in Table 3. Molar enthalpy of vaporization ΔH_v was calculated with the equation: $\Delta H_v =$

Table 1. Auxiliary quantities

Substance	Formula	ρ / g cm^{-3}	c_p / J K^{-1} g^{-1}	$-(\partial U/\partial p)_T$ / J MPa^{-1} g^{-1}	$-\{\Delta U_c^\circ/M\}$ / J g^{-1}
N,*N*-Dimethylaniline	$C_8H_{11}N$	0.9522	1.791	0.275	—
Liquid paraffin	$CH_{1.885}$	0.8824	2.22	0.257	45909.3±4.1[a]
Cotton fuse	$CH_{1.86}O_{0.93}$	1.5	1.70	0.29	16507

a) Uncertainty is the estimated sdm.

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Table 2. Combustion calorimetric results on *N*,*N*-dimethylaniline

Exptl	1	2	3	4
m'(compd)/g	0.23033	0.25878	0.24377	0.23743
m''(auxil)/g	0.41121	0.38376	0.40034	0.40886
m'''(fuse)/g	0.00156	0.00154	0.00150	0.00149
$m^i(H_2O)$/g	3.141	3.048	3.100	3.059
p^i(gas)/MPa	3.046	3.038	3.037	3.037
θ_i/°C	23.12339	23.12896	23.14412	23.12653
θ_f/°C	24.98875	24.98488	25.00985	25.00199
$\Delta\theta_{corr}$/°C	0.02196	0.02186	0.02012	0.02147
$n^f(HNO_3)$/mmol	0.402	0.436	0.415	0.387
ΔU_{ign}/J	6.3	4.1	5.2	4.2
ε^i(cont)/J K^{-1}	26.3	25.9	26.1	25.9
ε^f(cont)/J K^{-1}	27.9	27.4	27.7	27.5
ΔU_Σ	11.5	11.4	11.5	11.5
$-\Delta U_{IBP}$	27991.0	27850.8	28025.1	28153.2
$-\{\Delta U_c^\circ/M\}$/kJ g^{-1}	39.299	39.300	39.322	39.271
$-\Delta U_c^\circ$/kJ mol^{-1}	4762.4	4762.5	4765.1	4759.0

Table 3. Vaporization calorimetric results on *N*,*N*-dimethylaniline at 298.15 K

Exptl	$\frac{m}{\text{mg}}$	$\frac{t}{\text{s}}$	$\frac{I^{1)}}{\text{mA}}$	$\frac{\Delta H_v}{\text{kJ mol}^{-1}}$
1	31.55	1197.8	15.059	52.80
2	31.51	1197.4	15.059	52.85
3	31.62	1202.0	15.058	52.86
4	31.62	1200.9	15.053	52.78
5	31.60	1200.4	15.053	52.79
6	31.70	1205.1	15.060	52.88
7	31.64	1202.9	15.060	52.88
8	41.20	1797.5	15.050	52.82
9	41.34	1803.2	15.050	52.81

a) R(heater)=50.608 Ω.

$I^2Rt(M/m)$, where I is the current made to flow through the heater with the resistance R of 50.608 Ω at 298.15 K for the duration t, and, m and M are the mass and the molar mass, respectively, of the material vaporized during the experiment. Mean and sdm for the nine experiments were $(52.83\pm0.01_3)$ kJ mol^{-1}. Since the vapor pressure of *N*,*N*-dimethylaniline is much lower than 10^4 Pa at 298.15 K, ΔH_v, thus derived, may be taken to be ΔH_v°.

Derived standard thermodynamic quantities at 298.15 K are as follows: $\Delta U_c^\circ(1)=-(4762.2\pm3.2)$, $\Delta H_c^\circ(1)=-(4767.8\pm3.2)$, $\Delta H_f^\circ(1)=(47.7\pm3.4)$, $\Delta H_v^\circ=(52.83\pm0.03)$, and $\Delta H_f^\circ(g)=(100.5\pm3.4)$ kJ mol^{-1}, respectively, where uncertainties are the overall values. The overall standard deviation of mean for $\Delta U_c^\circ(1)$ and $\Delta H_c^\circ(1)$, $s(\bar{U})_\Sigma$, was calculated with the equation: $s(\bar{U})_\Sigma=\Delta U_c^\circ(1)[\sum_{i=1}^{4}\{f_i s_r(i)\}^2]^{1/2}$, where $s_r(i)$ and f_i are the relative standard deviation of mean and the weight, respectively, of the *i*-th contribution, which follows: (1) The experimental value of $\Delta U_c^\circ(1)$; (2) the energy equivalent; (3) the certified specific energy of combustion of the thermochemical standard benzoic acid; and (4) the specific standard energy of combustion of the paraffine oil. By letting $f_1=f_2=f_3=1$, $f_4=2$, $s_r(1)=2.7\times10^{-4}$, $s_r(2)=0.5\times10^{-4}$, $s_r(3)=0.4\times10^{-4}$, and $s_r(4)=0.9\times10^{-4}$, $s(\bar{U})_\Sigma$ was calculated to be 1.6 kJ mol^{-1}. The overall uncertainties for $\Delta U_c^\circ(1)$ and $\Delta H_c^\circ(1)$ are $\{2s(\bar{U})_\Sigma\}$. The following CODATA key values for thermodynamics[6] were used to calculate $\Delta H_f^\circ(1)$: $\Delta H_f^\circ(CO_2, g)=-(393.51\pm0.13)$ and $\Delta H_f^\circ(H_2O, 1)=-(285.830\pm0.042)$ kJ mol^{-1}, respectively, where uncertainties are those at the 95 per cent confidence level. The overall uncertainty for ΔH_v° is twice the sdm, $\{2s(\Delta H_v)\}$. The overall uncertainties for $\Delta H_f^\circ(1)$ and $\Delta H_f^\circ(g)$ are $[\{2s(\bar{U})_\Sigma\}^2+\{8\times0.13\}^2+\{5.5\times0.042\}^2]^{1/2}$ and $[\{2s(\bar{U})_\Sigma\}^2+\{8\times0.13\}^2+\{5.5\times0.042\}^2+\{2s(\Delta H_v)\}^2]^{1/2}$, respectively.

The large uncertainty assigned to $\Delta U_c^\circ(1)$ originates mainly from the relatively small masses of *N*,*N*-dimethylaniline used in the combustion experiments.

The only experimental value of $\Delta H_c^\circ(1)$ reported so far is the old value of Stohmann (-4782.4 kJ mol^{-1}),[7] while estimated values, *e.g.* -4754.3[8,9] and -4753.6[10] kJ mol^{-1}, respectively, are less negative than the old experimental value.[7] The present value is intermediate between the two groups. No other calorimetric value has been reported for ΔH_v°. The present value is higher than the value derived from the analysis of vapor pressure data, 49.8 kJ mol^{-1},[9] by 3.0 kJ mol^{-1}.

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