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Note

HEATS OF COMBUSTION AND FORMATION OF NORBORNANE *

AN XU-WU, ZHU HUI-PING and HU RI-HENG
Institute of Chemistry, Academia Sinica, Beijing (China)

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Norbornadiene and related compounds have recently received attention as model compounds for the study of solar-energy storage through valence-bond isomerization [1,2]. Extensive thermochemical investigations on the hydrogenation reactions of the norbornadiene system have been made. These include the heats of formation of these compounds derived from the heats of hydrogenation and the heat of formation of norbornane from combustion calorimetry [2–5]. The molecular mechanics method has also been employed to calculate their heats of formation [6,7]. A survey of the literature shows, however, that the experimental values of the heat of combustion of norbornane differ by about 10 kJ mol^{-1} and, therefore, a redetermination of this key value seemed desirable.

EXPERIMENTAL

Samples

Benzoic acid is the NBS 39i standard, for which the standard state heat of combustion is -26413.25 J g^{-1}. Norbornane (Aldrich Chemical Co.), after 3 vacuum sublimations, was purified by zone-melting (50 passes) under an N_2-atmosphere and finally collected by sublimation and dried with P_2O_5. It was pressed into pellets and sealed in thin polyester bags (0.025 mm thickness). They were placed under 40 atm. and tested for leaks. The heat of combustion of the polyester film had been determined previously ($\Delta E_c^0 = -22870.2 \pm 4.6$ J g^{-1}).

The purity of the norbornane sample was analyzed by g.l.c. (Varian 3700), with a 50 m FFAP quartz capillary column and flame ionization detector. The samples were dissolved in pure hexane and in α-pinene, respectively, and the solutions were injected for analysis. No apparent impurity peaks were observed. Its purity was estimated as > 99.95%.

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* Dedicated to Professor W.W. Wendlandt on the occasion of his 60th birthday.

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Apparatus

The basic construction of the precision rotation bomb calorimeter has been reported elsewhere [8]. Some important improvements have been made: an HP 2804A quartz thermometer is used to replace the original Pt-thermometer. A highly stable crystal oscillator made by the Chinese Academy of Meteorology was used as an external standard. A triple-point of water determination indicates that temperature measurements were reproducible to better than 0.0001 K. Two probes of the quartz thermometer are inserted respectively in the calorimeter can and the thermostat so that their respective temperatures and the difference can be measured. Sampling time in the combustion experiments was 10 s; the results were printed on a HP5050A printer. In temperature rise calculations, 10 consecutive measurements (100 s) were counted as one datum point for computer input. The calorimeter can contained 3500 g of water. The heats of stirring at different speeds were measured and a plot of the stirring heat vs. the cube of the stirring speed gave a straight line passing through the origin, indicating that the water evaporation had been effectively suppressed. The stirring speed was finally selected as 240 rpm. Within a single series of runs, the variation of Newton's cooling constant, k, was less than 0.3%. The main period of the run was so chosen that a longer period gave the same calculated cooling constant (to within 0.03%), stirring heat (to within 0.7%) and temperature rise (to within ± 0.00005 K). The calorimeter is able to operate in either isothermal or adiabatic modes. Both modes in the combustion experiment of squalane (used as an auxiliary combustion aid), give the same value and the same s.d.m. of five runs, equal to about $\pm 0.003\%$.

An LKB-8700 calorimetry system was used for the heat of sublimation measurement. The vaporization calorimeter of this system, as originally designed by Wadzo [9], is suitable for liquids, but for solids it becomes inconvenient for sample loading, and therefore was replaced by a new construction. The new calorimeter is similar in all respects to Wadso's original device, except that the base can be disassembled and a Teflon ring is used to achieve tight sealing. The base where the heater is embedded and the lower side of the calorimeter are covered with a close-fitting casing made of thin aluminium sheeting to improve the thermal contact between the two parts. Experiments with water gave $\Delta H_v^0(H_2O) = 43.95 \pm 0.14$ kJ mol^{-1}, indicating that it works satisfactorily.

Combustion experiments

In this series of measurement, the calorimeter operated in the isothermal mode. One gram of water was placed in the bomb whose volume is 224.66 cm^3. The oxygen pressure was 40 atm*. Poly-propylene thread was used for

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* 1 atm = 101325 Pa.

ignition, its heat of combustion being determined in a separate experiment and equal to -46119.0 ± 4.1 J g^{-1}. The thermostat temperature was 25.20 ± 0.001°C. Starting temperature of the calorimeter was 23.5°C. The temperature rise was 1.5 K. In the combustion experiments with norbornane, benzoic acid was added to give the same temperature rise. The rotating mechanism was not used in this study; otherwise the procedures of the experiment were the same as those reported in the literature [8].

At the end of each combustion experiment, a CO test was made for bomb gas (He-bi Coal Co. Quick CO identification tube) and was found to be satisfactory. In two runs of the series, minute quantities of soot (0.00016 and 0.00002 g respectively) were observed in the crucible and corrected for by weight. Liquid in the bomb was rinsed out for HNO_3 analysis after the combustion.

RESULTS

The experimental data were processed by an HP9835A computer with a program obtained by courtesy of Lund University, Sweden (with some modifications by us). Atomic masses of 1977 were adopted for molecular mass calculations. Values for Henry's Law constant, $k(CO_2) = 0.03414$ mol dm^{-3} atm^{-1}, and for $\Delta E_{soln}(CO_2, g) = -17280 \pm 167$ J mol^{-1} were taken from ref. 8.

The auxiliary data used in the calculations are listed in Table 1. Results from a typical combustion experiment are shown in Table 2. The results of five consecutive combustion experiments, and the results of sublimation experiments are given in Table 3. A comparison of our results and those of Bedford et al. [5], and of Steele [2] is made in Table 4. The standard enthalpy of combustion at 298.15 K refers to the enthalpy of reaction of the following idealized combustion reaction at that temperature

$$C_7H_{12}(c) + 10O_2(g) = 7CO_2(g) + 6H_2O(l) \qquad \Delta H_c^0$$

The values of $\Delta H_f^0(CO_2, g)$ and $\Delta H_f^0(H_2O, l)$ used in computing the enthalpy of formation of the compound are the same as in ref. 8.

TABLE 1

Auxiliary data used in the calculations

Compounds	ρ (g cm^{-3})	$(\partial V/\partial T)_p$ (mm^3 K^{-1} g^{-1})	C_p (J K^{-1} g^{-1})
Benzoic acid	1.32	0.43	1.20
Norbornane	1.09	–	1.57
Polyester film	1.38	–	1.32

TABLE 2

Summary of a typical combustion experiment

	Benzoic acid	Norbornane
m(Compd) (g)	0.975833	0.405298
m(Aux B.A.) (g)	0	0.282497
m(Film) (g)	0	0.028781
m(PPL) (g)	0.001020	0.001260
ϵ^{i}(Cont) (J K^{-1})	16.10	15.97
$\Delta\theta$ (K)	1.44502	1.48720
w(Ign) (J)	-0.24	-0.31
$\Delta E^{f}_{dec}(HNO_3)$ (J)	0.06	0.88
$\Delta E^{f}_{soln}(CO_2)$ (J)	4.05	3.85
ΔE_{Σ} (J)	27.13	17.52
$\epsilon^{0}(\text{Calor})_{1.2}$ (J K^{-1})	17872.78	17872.94
ΔE^{0}_{c}(Compd) (J g^{-1})	-26413.25	-45416.02

TABLE 3

Results of combustion and sublimation experiments

Benzoic acid	Norbornane	
$\epsilon^{0}(\text{Calor.})_{1.2}$ (J K^{-1})	$-\Delta E^{0}_{c}$(Compd.) (J g^{-1})	ΔH^{0}_{s}(kJ mol^{-1})
17872.78	45416.0	39.81
17873.91	45396.8	39.99
17872.75	45406.6	40.22
17872.70	45422.1	40.29
17872.57	45407.8	39.91
Mean 17872.94	45409.8	40.04
s.d.m. ±0.24	±4.3	±0.09

TABLE 4

Results and derived quantities at 298.15 K and comparison with literature data (kJ mol^{-1})

Author	Year	$-\Delta E^{0}_{c}$(s)	$-\Delta H^{0}_{c}$(s)	$-\Delta H^{0}_{f}$(s)	ΔH^{0}_{s}	$-\Delta H^{0}_{f}$(g)
An Xu-wu	1986	4367.14	4374.59	94.96	40.04	54.92
et al.		±0.97	±0.97	±1.05	±0.18	±1.06
A.F. Bedford	1963	4370.02	4377.47	92.09		52.05
et al.		±2.18	±2.18	±2.72		±2.73
W.V. Steele	1978	4360.1	4367.5	102.0		62.0
		±3.3	±3.3	±3.3		±3.3

(Uncertainties = $2S_{\text{over-all}}$)

Using the enthalpy of sublimation data measured in this study, the enthalpy of formation of norbornane in the gaseous state was obtained and is given in Table 4.

DISCUSSION

In 1963, Bedford et al. [5] determined the standard energy of combustion of norbornane (purity > 99.9%), $\Delta E_c^0 = -4370.02 \pm 2.18$ kJ mol^{-1}. In 1978, Steele [2] redetermined this quantity, finding $\Delta E_c^0 = -4360.1 \pm 3.3$ kJ mol^{-1} (purity > 99.95%). Our result (purity > 99.95%) of $\Delta E_c^0 = -4367.14 \pm 0.97$ kJ mol^{-1} lies between these two values, but closer to the former one. In fact, the value obtained by Bedford et al. agrees with ours within experimental error. The purity of all the samples used in these three determinations is satisfactory; our calorimeter, however, has the highest precision (in calibration experiments, the s.d.m. of the Bedford et al. study is ±0.014%; that of Steele is ±0.037%; ours is ±0.003%), and therefore our result has the smallest uncertainty.

In this study, the enthalpy of sublimation of norbornane was obtained directly by calorimetry and is, therefore, expected to be more precise and reliable than the literature data (40.4 ± 0.8 kJ mol^{-1}) which was derived from vapour pressure measurements.

Allinger et al. have calculated the enthalpy of formation of norbornane in the gas state by the molecular mechanical method. Their modified MM1 field [6] gives $\Delta H_f^0(\mathrm{g}) = -56.11$ kJ mol^{-1} and their MM2 field [7] gives $\Delta H_f^0(\mathrm{g}) = -53.72$ kJ mol^{-1}. Their calculated values agree closely with our result. Wiberg [10], using an ab initio quantum mechanical method, obtained $\Delta H_f^0(\mathrm{g}) = -56.65$ kJ mol^{-1}.

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