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Enthalpies of Combustion and Formation of 1,4-Dihydro-1,4-epoxynaphthalene

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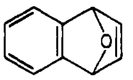
Measurement was made of the enthalpy of combustion of 1,4-dihydro-1,4-epoxynaphthalene, $C_{10}H_8O$ (crystal). The standard enthalpies of combustion and formation were calculated for 298.15 K: $\Delta H_c^\circ = -5140.5 \pm 5.7$ kJ mol^{-1} $= -1228.61 \pm 1.36$ kcal mol^{-1}; $\Delta H_f^\circ = 62.1 \pm 5.8$ kJ $mol^{-1} = 14.84 \pm 1.39$ kcal mol^{-1}. The enthalpy of decomposition at 298.15 K of this solid compound into solid naphthalene and gaseous molecular oxygen was calculated to be $\Delta H^\circ = 3.82 \pm 1.41$ kcal mol^{-1}, and, into solid naphthalene and gaseous atomic oxygen, $\Delta H^\circ = 63.4 \pm 1.4$ kcal mol^{-1}.

The compound 1,4-dihydro-1,4-epoxynaphthalene, $C_{10}H_8O$, which has the structure



is of interest as an oxidizing agent with unusual properties. One would expect the release of oxygen from this compound to require much less energy than in the case of most epoxides because, in the process, an aliphatic ring is converted to an aromatic ring. For a quantitative consideration of the energetics of this compound, a knowledge of its enthalpy of formation is needed.

Synthesis and Purification

The 1,4-dihydro-1,4-epoxynaphthalene, $C_{10}H_8O$ (crystal), was prepared following the procedures of Fieser and Haddadin (*6*) and Ziegler (*12*). The compound was recrystallized twice from *n*-hexane and then sublimed. It was analyzed by gas chromatography and stored for 5 months in a tightly capped bottle in the dark at temperatures not exceeding 301 K. The combustion measurements were then made and the remaining material was analyzed again, about 2 weeks later.

Portions of the sample were pale yellow, while others were white. The white appearance is ascribed to a smaller crystallite size, which makes the natural color of the material more difficult to see. Portions of the sample had a "sticky" texture. This is ascribed to the formation of very small amounts of impurity-rich liquid at temperatures below the melting point of the pure compound. The portions of the sample selected for combustion work were free from "stickiness" and were mostly white.

The initial analysis showed no impurities under conditions such that 0.1% impurity would have been detectable. The final analysis was made under gas chromatographic conditions allowing greater sensitivity and showed 0.14 ± 0.02% of 1-naphthol and no other impurities; the undetected impurities are estimated as less than 0.05%.

Calorimetric Apparatus and Procedures

The calorimetric apparatus and procedures were the same as previously reported (*4*, *5*, *7*), with the ignition system and values for the energy of ignition being the same as in ref 5. The paraffin oil, TKL-66, the same as used previously (*4*), had been sealed in a glass container and stored in an opaque outer container in an area not subject to extremes of temperature. For these experiments, its energy of combustion was taken from the earlier experiments (*4*). The final temperature in each combustion experiment was 298.15 K within 0.02 K. The amount of reaction in each combustion experiment was determined from the mass of sample, with appropriate correction to mass under vacuum. The values of the atomic weights and molecular weight used were as follows (*3*): C, 12.011; H, 1.0079; O, 15.9994; $C_{10}H_8O$, 144.1726.

The energy equivalent of the standard calorimeter system, ϵ_s, was determined using standard benzoic acid, U.S. National Bureau of Standards No. 39i, which was certified to have a specific energy of combustion at 298.15 K of 26 434 ± 3 J g^{-1}, under the conditions specified in the certificate, including the correction for nitric acid formed, as 59 kJ mol^{-1}. In one of the experiments with benzoic acid, the fuse wire burned completely.

The $C_{10}H_8O$ was burned in the form of unconfined pellets. In the first experiment, insignificant traces of soot and carbon monoxide were formed. In the second experiment, large amounts of soot, carbon monoxide, and unburned material were found in the bomb after combustion. The reaction was so rapid and violent that a drop of molten fuse struck the lid of the bomb. For the protection of the bomb and the economical use of time and material, auxiliary oil was added to the pellets in the remaining four experiments to reduce the rate of combustion. No

Table I. Results of Five Experiments to Determine ϵ_s, the Energy Equivalent of the Calorimeter System

m_{BA}/g	$10^5 K/s^{-1}$	$10^4 u$/-K min^{-1}	Δt/K	Δt_c/K	$(\epsilon - \epsilon_s)$/J K^{-1}	q_n/J	q_i/J	ϵ_s/J K^{-1}
1.14270–1.15425	3.28–3.38	1.27–1.75	1.9919–2.0125	1.98372–2.00449	19.36–19.39	0.32–2.43	64.77–74.73	15239.92–15245.20
1.14809[a]			2.0015[a]	1.99326[a]	19.37[a]	0.82[a]	70.40[a]	15242.31[a,b]

[a] Mean value. [b] Standard deviation of the mean: ±0.94.

Table II. Results of Five Measurements of the Energy of Combustion of Solid 1,4-Dihydro-1,4-epoxynaphthalene, at 298.15 K

m_{sample}/g	$10^5 K/s^{-1}$	$10^4 u$/-K min^{-1}	Δt/K	Δt_c/K	E/J K^{-1}	q_{oil}/J	q_n/J	q_i/J	q_{im}/J	ΔE_c/J mol^{-1}
0.42484–0.81542	3.34–3.44	1.11–1.91	1.9182–2.0717	1.90943–2.06461	15261.66–15261.81	0.00–16081.26	1.93–3.41	64.06–75.78	−0.72 to −1.38	5136.95 5143.91
0.50701[a]			1.9786[a]	1.97063[a]	15261.73[a]	11928.41[a]	2.61[a]	70.42[a]	−0.86[a]	5139.61[a,b]

[a] Mean value. [b] Standard deviation of the mean: ±1.15.

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soot or carbon monoxide was formed during these experiments with auxiliary oil. The fuse wire burned completely in one of the five experiments.

Results and Calculations

Table I gives the results of the five experiments to determine the energy equivalent of the standard calorimeter system. Table II gives the results of the five experiments on the combustion of $C_{10}H_8O$. The symbols used in these tables are the same as in earlier reports (*4*, *5*, *8*, *9*), and the manner of calculation and presentation of the data is explained in (*8*, *9*).

Applying the Washburn correction, 3.07 kJ mol^{-1}, to the value of ΔE_c (from Table II) to obtain ΔE_c° and using the recommended values for the standard enthalpies of formation of water and carbon dioxide (*1*), we obtain the following for $C_{10}H_8O(c)$ at 298.15 K:

$$\Delta E_c^\circ = -5136.78 \pm 2.30 \text{ kJ mol}^{-1}$$

$$\Delta H_c^\circ = -5140.5 \pm 5.7 \text{ kJ mol}^{-1} = -1228.61 \pm 1.36 \text{ kcal mol}^{-1}$$

$$\Delta H_f^\circ = 62.1 \pm 5.8 \text{ kJ mol}^{-1} = 14.84 \pm 1.39 \text{ kcal mol}^{-1}$$

The foregoing uncertainties are taken as twice the propagated standard deviation of the mean, including the following components, as appropriate: (a) for the certified value of the standard benzoic acid, ±0.004%; (b) for the determination of the energy equivalent of the standard calorimeter system (Table I); (c) for the combustion experiments on $C_{10}H_8O$ (Table II); (d) for the effect of unknown impurities, ±0.05%. One calorie is taken as exactly 4.184 J.

Using the previously selected value for the standard enthalpy of formation of naphthalene (*2*, *8*, *10*), $\Delta H_f^\circ = 18.66 \pm 0.23$ kcal mol^{-1} at 298.15 K, and the value for the dissociation of oxygen into its atoms recommended by Wagman et al. (*11*), $\Delta H^\circ = 119.10 \pm 0.01$ kcal mol^{-1} at 298.15 K, the standard enthalpy for the dissociation of $C_{10}H_8O(c)$ into naphthalene and molecular oxygen and into naphthalene and atomic oxygen was calculated as follows, at 298.15 K:

$$C_{10}H_8O(c) = C_{10}H_8(c) + {}^1/_2O_2(g); \quad \Delta H^\circ = 3.82 \pm 1.41 \text{ kcal mol}^{-1}$$

$$C_{10}H_8O(c) = C_{10}H_8(c) + O(g); \quad \Delta H^\circ = 63.4 \pm 1.4 \text{ kcal mol}^{-1}$$

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Study of Vapor Pressure and Critical Properties of Perfluoro-*n*-hexane

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The vapor pressure of perfluoro-*n*-hexane was determined from 160 °C to the critical point and correlated by an equation. The critical properties were measured and compared with the most reliable values reported in literature.

Introduction

A lot of work has been done on binary systems containing perfluoro-*n*-hexane (*1*, *5*, *11*) but little work (*6*) has been done on the study of perfluoro-*n*-hexane of high purity. Burger and Cady (*2*) and Stiles and Cady (*10*) studied some physical properties of perfluoro-*n*-hexane but the purity of their sample was estimated by them to be 96.5 mol % pure. Crowder et al. (*4*) studied the vapor pressure from low pressure to the critical point, and they obtained two equations, one for pressures less than atmospheric pressure and the other for pressures to the critical value.

The objective of this work is to measure vapor pressure data and correlate them with an equation. Also to measure the critical properties and compare them with the most reliable values reported by Kudchodker, Alani, and Zwolinski (*8*).

Experimental Section

Perfluoro-*n*-hexane was supplied by Pierce Chemical Co. who stated that the purity is 98+%. The sample was further purified by placing it in contact with activated molecular sieves to absorb

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