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The determination of the heats of combustion and the resonance energies of some substituted naphthalenes

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Abstract

In this study, some heats of combustion and resonance energies for 1-substituted naphthalenes have been determined.

The heats of combustion of naphthalene, 1-naphthol, 1-naphthylamine, 1-methylnaphthalene, 1-fluoronaphthalene, 1-naphthylacetate and 1-naphthoic acid were determined as 1230.90 ± 1.23, 1183.34 ± 1.18, 1263.35 ± 1.26, 1382.17 ± 1.38, 1217.97 ± 1.22, 1383.92 ± 1.38, and 1221.49 ± 1.22 kcal mol^{-1} respectively. The resonance energies of naphthalene, 1-naphthol, 1-naphthylamine and 1-methylnaphthalene were calculated to be 74.0 ± 1.2, 73.6 ± 1.2, 53.5 ± 1.3, and 95.4 ± 1.4 kcal mol^{-1} respectively.

Keywords: Heat of combustion; Resonance energy; 1-substituted naphthalenes

1. Introduction

In this study, the heats of combustion of several substituted naphthalenes have been determined using an adiabatic bomb calorimeter, and resonance energies of these compounds were calculated using heats of combustion. 1-Substituted naphthalenes were selected to investigate the effects on the resonance energies of substituent groups.

Although there are a great number of theoretical studies of resonance energies of non-substituted conjugated aromatic compounds, experimental studies are limited [1–19]. Furthermore, there are few works on the resonance energies of substituted

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conjugated aromatic compounds [20–30]. Calorimetry is a technique for measuring heat change. Several types of calorimeters have been devised, and adaptions have been made for special purpose [1, 2, 20, 31–40].

A quantitative measure of the stabilization of a delocalized molecule is provided by its resonance energy, which is defined as the difference in the energy between the delocalized and localized ∏-electron systems.

The resonance energy of a substance $C_aH_bO_cN_dS_eCl_fBr_gI_hF_j$ can be calculated from the heat of combustion and also from other heats of reactions.

The reaction of the combustion of this substance is shown as follows [22]

$$\begin{aligned} &C_aH_bO_cN_dS_eCl_fBr_gI_hF_j(g) + \left[a + \frac{b-f-j}{4} + e - \frac{c}{2}\right]O_2(g) \\ &\rightarrow aCO_2(g) + \frac{b-f-j}{2}H_2O(l) + \frac{d}{2}N_2(g) + eSO_2(g) \\ &+ fHCl(g) + \frac{g}{2}Br_2(g) + \frac{h}{2}I_2(s) + jHF(g) + \Lambda\,\mathrm{kcal\,mol^{-1}} \end{aligned} \tag{1}$$

The decomposition reaction of $C_aH_bO_cN_dS_eCl_fBr_gI_hF_j$ is

$$\begin{aligned} C_aH_bO_cN_dS_eCl_fBr_gI_hF_j(g) \rightarrow\ & aCl(g) + bH(g) + cO(g) \\ & + dN(g) + eS(g) + fCl(g) \\ & + gBr(g) + hI(g) + jF(g) \\ & + E\,\mathrm{kcal\,mol^{-1}} \end{aligned} \tag{2}$$

We can obtain the energy E from the combustion reactions and the following other reactions

$$aCO_2(g) \rightarrow aC\ (\mathrm{graphite}) + aO_2(g) - 94.1a\ \mathrm{kcal} \tag{3}$$

$$aC\ (\mathrm{graphite}) \rightarrow aC(g) - 171.7a\ \mathrm{kcal} \tag{4}$$

$$\begin{aligned} [(b-f-j)/2]H_2O(l) \rightarrow [(b-f-j)/2]\,H_2(g) + [(b-f-j)/4]\,O_2(g) \\ - 34.2(b-f-j)\ \mathrm{kcal} \end{aligned} \tag{5}$$

$$(b/2)H_2(g) \rightarrow bH(g) - 52.1b\ \mathrm{kcal} \tag{6}$$

$$(c/2)O_2(g) \rightarrow cO(g) - 59.2c\ \mathrm{kcal} \tag{7}$$

$$(d/2)N_2(g) \rightarrow dN(g) - 85.6d\ \mathrm{kcal} \tag{8}$$

$$eSO_2(g) \rightarrow eS(\mathrm{rhombic}) + eO_2(g) - 71.0e\ \mathrm{kcal} \tag{9}$$

$$eS(\mathrm{rhombic}) \rightarrow eS(g) - 53.3e\ \mathrm{kcal} \tag{10}$$

$$fHCl(g) \rightarrow (f/2)H_2(g) + (f/2)Cl_2(g) - 22.1f\ \mathrm{kcal} \tag{11}$$

$$(f/2)Cl_2(g) \rightarrow fCl(g) - 29.0f\ \mathrm{kcal} \tag{12}$$

$$(g/2)Br_2(g) \rightarrow gBr(g) - 26.7g\ \mathrm{kcal} \tag{13}$$

$$(h/2)I_2(s) \rightarrow hI(g) - 25.5\,h \text{ kcal} \tag{14}$$

$$jHF(g) \rightarrow (j/2)H_2(g) + (j/2)F_2(g) - 64.2j \text{ kcal} \tag{15}$$

$$(j/2)F_2(g) \rightarrow jF(g) - 18.3j \text{ kcal} \tag{16}$$

If we add Eq. (1) to Eqs. (3)–(16) we get

$$\begin{aligned} C_aH_bO_cN_dS_eCl_fBr_gI_hF_j(g) \rightarrow\ & aC(g) + bH(g) + cO(g) \\ & eS(g) + fCl(g) + gBr(g) \\ & hI(g) + jF(g) + \Lambda \\ & -(265.8a + 86.3b + 59.2c \\ & + 85.6d + 124.3e + 16.9f \\ & + 26.7g + 25.5\,h + 48.3j) \text{ kcal} \end{aligned} \tag{17}$$

Comparison of the right-side of Eq. (17) with Eq. (2) leads to

$$\begin{aligned} E = \Lambda - (& 265.8a + 86.3b + 59.2c + 85.6d \\ & + 124.3e + 16.9f + 26.7g + 25.5h + 48.3j) \text{ kcal} \end{aligned} \tag{18}$$

The energy E can be written as the total energy of the chemical bonds of the molecule

$$E = -\sum D_i(A - B) \tag{19}$$

The energies of E and Λ belong to the molecule in the gas phase, and Λ is the theoretical combustion energy. If the molecule is in the solid or liquid phase, we must take account the phase transition enthalpies

$$\Delta H_{gas}(\text{combustion}) = \Delta H_{solid}(\text{combustion}) + \Delta H'(\text{phase transition}) \tag{20}$$

Thus, the energy of resonance is

$$\text{R.E.} = \Lambda(\text{theoretical}) - \Delta H(\text{experimental}) \tag{21}$$

The values of Λ and ΔH must be taken at 25°C.

2. Experimental

2.1. Chemicals and equipment

Benzoic acid (National Bureau of Standards, Gaithersburg), naphthalene (> 99%), 1-naphthol (> 99%), 1-naphthylamine (> 99%), 1-naphthoic acid (99%), 1-fluoronaphthalene (99%), 1-methylnaphthalene (98%) and 1-naphthylacetate (98%) were purchased from Merck, Darmstad or Aldrich Chemical Co., Milwaukee. All chemicals were used as received. Solid chemicals were compressed into a pellet and liquid chemicals were put in an acetobutyrate capsule before combustion. The heats of combustion were measured using an IKA C 400 model adiabatic calorimeter. The changes in temperature were measured with a Beckman thermometer.

2.2. Method

The total heat capcity of the calorimeter and its contents were determined using benzoic acid which has a well-known heat of combustion. The total heat capacity (C) of the calorimeter was calculated from the equation

$$C = \frac{H_B M_B + Q_w l}{\Delta t} \tag{22}$$

where H_B, the combustion enthalpy of benzoic acid, is 26464 ± 3 J g^{-1} at 25°C, M_B is the weight of combusted benzoic acid, Q_w is the heat of combustion of the wire used in experiments which is 6.3 J cm^{-1}, l is the length of combusted wire, and $\Delta t = t_2 - t_1$, where t_2 is the final temperature and t_1 is the initial temperature.

The procedure used for the determination of the total heat capacity of the calorimeter and its content was repeated for all of the other experiments. In the experiments, five ml of water was placed in the bottom of the bomb. The bomb was filled and emptied three times with O_2 gas at 30 atm. The room temperature was held constant at 25°C during the experiment.

After the combustion reaction, the residual liquid in the bomb was titrated with a standard solution of NaOH using methyl orange indicator. Then the number of moles of HNO_3, which was formed from the nitrogen impurity in the oxygen gas, was calculated. This gave a value of 4.0×10^{-4} moles for every experiment

$$1/2N_2(g) + 5/4O_2(g) + 1/2H_2O(l) \rightarrow HNO_3(aq) \tag{23}$$

The heat of this reaction [20] is 57.8 kJ mol^{-1}. The heat of 4.0×10^{-4} mol HNO_3 was calculated as 0.023 kJ mol^{-1}. This represents 0.86% of the heat of combustion of the benzoic acid which was used in these experiments.

The heat of formation of HNO_3(aq) was assumed to be negligible for calculating the capacity of the calorimeter.

The capacity of the calorimeter was determined as 9893.19 ± 3.69 J K^{-1}. The C_p values of the studied chemicals were obtained or calculated from the literature. As the enthalpies of combustion of 1-naphthylamine and 1-fluoronaphthalene were determined, all substituted groups in the molecules such as amine and fluoride could be expected to contribute to the total heat to some extent, due to the fact that the formation of HNO_3 and HF caused the total heat in the bomb after the combustion process to rise. To calculate properly the heats of combustion of each molecule individually, it is obvious that the heats of formation of HNO_3 and HF should be subtracted from the heats of combustion of 1-naphthylamine and 1-fluoronaphthalene respectively.

3. Results and discussion

Naphthalene has the following properties: melting point, 80.5°C; boiling point, 218°C; C_p(solid) = 1.176 J $g^{-1}K^{-1}$ + $0.464 \times 10^{-2}T$ J $g^{-1}K^{-2}$ [25]; C_p(liquid) = 1.684 J g^{-1} K^{-1} [25]; C_p(gas) = −53.51 J mol^{-1} K^{-1} + 0.703 T J mol^{-1} K^{-2} − $347.4 \times 10^{-6} T^2$ J mol^{-1} K^{-3} (this value was calculated from literature data [21]); $\Delta H_{\mathrm{M}}^{T_{\mathrm{M}}}$ (enthalpy of melting) = 18776.45 J mol^{-1} [26]; $\Delta H_{\mathrm{V}}^{T_{\mathrm{B}}}$ (enthalpy of vaporization) = 71400.79 J mol^{-1} [26]. The reaction of combustion of naphthalene is

$$C_{10}H_8(\mathrm{s}) + 12O_2 \rightarrow 10CO_2(\mathrm{g}) + 4H_2O(\mathrm{l})$$

$$\Delta E + Q_{\mathrm{W}} = C\Delta t \qquad (24)$$

The value of ΔE has been calculated from Eq. (24). In this study, ΔE was determined to be 5155.05 ± 5.16 kJ mol^{-1}. The enthalpy of combustion (ΔH) at constant pressure was calculated from the known value of ΔE: $\Delta H = \Delta E + \Delta nRT$, where Δn is the difference between the numbers of gas molecules of reactants and products in the combustion reaction, $\Delta n = nCO_2 - nO_2 = -2$. The value of ΔH in the solid phase was calculated to be 5150.09 ± 5.15 kJ mol^{-1} at 25°C.

$$\Delta H_{\mathrm{gas}}^{25^{\circ}\mathrm{C}} = \Delta H_{\mathrm{solid}}^{25^{\circ}\mathrm{C}} + \Delta H_{\mathrm{M}}^{T_{\mathrm{M}}} \int_{T_{\mathrm{M}}}^{25^{\circ}\mathrm{C}} [C_{\mathrm{p}}(\mathrm{l}) - C_{\mathrm{p}}(\mathrm{s})]\mathrm{d}T + \Delta H_{\mathrm{V}}^{T_{\mathrm{B}}} +$$

$$+ \int_{T_{\mathrm{B}}}^{25^{\circ}\mathrm{C}} [C_{\mathrm{p}}(\mathrm{g}) - C_{\mathrm{p}}(\mathrm{l})]\mathrm{d}T$$

$$C_p(\mathrm{g}) - C_p(\mathrm{l}) = -268.86 + 0.703\,T - 347.4 \times 10^{-6}\,T^2$$

$$C_p(\mathrm{l}) - C_p(\mathrm{s}) = 65.02 - 0.5939\,T$$

$$\Delta H_{\mathrm{gas}}^{25^{\circ}\mathrm{C}} = 5256.36 \pm 5.15\ \mathrm{kJ\ mol^{-1}}$$

Thus using Eqs. (2) and Eq. (17) for naphthalene

$$C_{10}H_8(\mathrm{g}) \rightarrow 10C(\mathrm{g}) + 8H(\mathrm{g})$$

$$E_{\mathrm{gas}}^{25^{\circ}\mathrm{C}} = \Lambda_{\mathrm{gas}}^{25^{\circ}\mathrm{C}} - (265.8a + 86.3\,b)\ \mathrm{kcal\ mol^{-1}} \quad a = 10, b = 8$$

$$E_{\mathrm{gas}}^{25^{\circ}\mathrm{C}} = -\sum D_i(\mathrm{A} - \mathrm{B}) = -[5(\mathrm{C{=}C}) + 6(\mathrm{C-C}) + 8(\mathrm{C-H})]$$

$$= \Lambda_{\mathrm{gas}}^{25^{\circ}\mathrm{C}} - 3348.4$$

Bond energies [27] (kcal mol^{-1}) are: C=C, 146.27; C – C, 83.17; C – H, 98.47.

$$\Lambda_{\mathrm{gas}}^{25^{\circ}\mathrm{C}} = 1330.27\ \mathrm{kcal\ mol^{-1}} = 5565.85\ \mathrm{kJ\ mol^{-1}}$$

Resonance energy = $5565.85 - 5256.36 = 309.49 \pm 5.15$ kJ mol^{-1} = 74.0 ± 1.2 kcal mol^{-1}

In related literature [24], the value of the resonance energy of naphthalene is given as 75 kcal mol^{-1}; therefore the above method may be accepted as reliable. The other results obtained for the substituted naphthalenes are listed in Tables 1 and 2.

In this work, naphthalene was chosen as a control and comparison substance because its enthalpy of combustion and resonance energy are known. All of the values of the heat capacities and the heats of phase transition for the investigated substances are necessary for calculations. As there was insufficient data, in some cases the resonance energies for all the included substances were not calculated. For 1-methyl-

Table 1
Physical and chemical data of some substituted naphthalenes

Naphthalene derivative	Literature data and experimental results ($C_p = A + BT + CT^2 + \cdots$) A/J mol^{-1} K^{-1}, B/J mol^{-1} K^{-2}, C/J mol^{-1} K^{-3}	Ref.
Naphthalene	C_p(solid) = 150.75 + 0.5948 T	[25]
(solid)	C_p(liquid) = 215.87	[25]
$C_{10}H_8$	C_p(gas) = − 53.31 + 0.703 T − 347.10^{-6} T^2	[21]
	Melting point, 80.5°C	
	Boiling point, 218°C	
	Heat of fusion, 18.776 kJ mol^{-1}	[26]
	Heat of vaporization, 71.401 kJ mol^{-1}	[26]
	$\Delta H^{25^\circ C}_{gas}$(Combustion), 5256.36 + 5.15 kJ mol^{-1}	
	$\Lambda^{25^\circ C}_{gas}$(Combustion, theoretical), 5565.85 kJ mol^{-1}	[22,27]
1-Naphthol	C_p(solid) = 144.76 + 0.8867 T	[25]
(solid)	C_p(liquid) = 234.45 + 0.46 T	[25]
$C_{10}H_8O$	C_p(gas) = − 45.73 + 0.742 T − 2.97 × 10^{-4} T^2	[21]
	Melting point, 96°C	
	Boiling point, 288°C	
	Heat of fusion, 23.492 kJ mol^{-1}	[36]
	Heat of vaporization, 59.436 kJ mol^{-1}	[26]
	$\Delta H^{25^\circ C}_{gas}$(Combustion), 5094.46 ± 4.95 kJ mol^{-1}	
	$\Lambda^{25^\circ C}_{gas}$(Combustion, theoretical), 5402.55 kJ mol^{-1}	[22,27]
1-Naphthylamine	C_p(solid) = 161.80 + 1.86 T	[25]
	C_p(liquid) = 280.08 + 1.396 × 10^{-2} T	[25]
(solid)	C_p(gas) = − 54.52 + 0.772 T − 3.81 × 10^{-4} T^2	[21]
$C_{10}H_9N_2$	Melting point, 50°C	
	Boiling point, 300.8°C	
	Heat of fusion, 13.384 kJ mol^{-1}	[26]
	Heat of vaporization, 60.789 kJ mol^{-1}	[26]
	$\Delta H^{25^\circ C}_{gas}$(Combustion), 5392.13 ± 5.29 kJ mol^{-1}	
	$\Lambda^{25^\circ C}_{gas}$(Combustion, theoretical), 5616.10 kJ mol^{-1}	[22,27]
1-Methylnaphthalene	Boiling point, 244.6°C	
	Heat of vaporization, 46.024 kJ mol^{-1}	[28]
(liquid)	Heat of vaporization (at 25°C), 58.314 kJ mol^{-1}	[28]
$C_{11}H_{10}$	$\Delta H^{25^\circ C}_{gas}$(Combustion), 5829.02 ± 5.83 kJ mol^{-1}	
	$\Lambda^{25^\circ C}_{gas}$(Combustion, theoretical), 6228.02 kJ mol^{-1}	[22,27]
1-Fluoro-naphthalene	C_p(liquid) = –	[21]
(liquid) $C_{10}H_7F$	C_p(gas) = − 52.93 + 72.95 × 10^{-2} T − 18.14 × 10^{-5} T^2	
	Heat of vaporization, –	
1-Naphthylacetate	C_p(solid) = –	
	C_p(liquid) = –	
(solid)	C_p(gas) = − 31.21 + 0.941 T − 0.435 × 10^{-3} T^2	[21]
$C_{12}H_{10}O_2$	Melting point, 45°C	
	Boiling point	
	Heat of fusion, –	
1-Naphthoic	C_p(solid) = –	
acid	C_p(liquid) = –	
(solid)	C_p(gas) = − 38.26 + 0.814 T − 0.418 × 10^{-3} T^2	[21]
$C_{11}H_8O_2$	Melting point, 161°C	
	Boiling point, –	
	Heat of vaporization, 94.480 kJ mol^{-1}	[26]

Table 2
Enthalpies of combustion and resonance energies of some substituted naphthalenes

Naphthalene derivative	$\Delta H^{25\,\mathrm{C}}$(combustion)/kcal mol^{-1}		Resonance energy/kcal mol^{-1}	
	This work	Literature	This work	Literature
Naphthalene		1231.8 [26]		61.0 [22]
(solid)		1249.7 [22]		75.0 [24]
	1230.90 ± 1.23	1229.3 [23]	74.0 ± 1.2	
		1232.54 [23]		
		1230.20 [23]		
		1232.35 [23]		
1-Naphthol		1185.4 [26]		
(solid)	1183.34 ± 1.18	1186.81 [23]	73.6 ± 1.2	–
		1184.84 [23]		
1-Naphthylamine		1263.5 [26]		
	1263.35 ± 1.26	1283.6 [22]	53.5 ± 1.3	64 [22]
(solid)		1264.1 [23]		
1-Methylnaphthalene (liquid)	1382.17 ± 1.38	–	95.4 ± 1.4	–
1-Fluoronaphthalene (liquid)	1217.97 ± 22	–	–	–
1-Naphthylacetate		1401.30 [23]		
	1383.92 ± 1.38	1397.30 [23]	–	–
(solid)				
1-Naphthoic				
acid	1221.49 ± 1.22	1231.8 [26]	–	–
(solid)		1228.11 [23]		

naphthalene, the calculation of $\Delta H_{\mathrm{V}}^{25\,\mathrm{C}}$ was made using gas phase values of the C_{p} determined by spectroscopic data and with the aid of the Kirchoff equation. The obtained result is very close to the previously reported literature value [28]. Whichever value of $\Delta H_{\mathrm{V}}^{25\,\mathrm{C}}$ was used, no effect was seen in the value of the resonance energy.

From these results, it can be seen that electron delocalization in 1-methylnaphthalene can occur more readily than in unsubstituted naphthalene. In contrast, the amine group at the same position on the naphthalene decreases the resonance energy of the naphthalene molecule.

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