Enthalpies of Combustion and Sublimation and Vapor Pressures of Three Benzoquinolines

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The enthalpies of combustion and sublimation and the vapor pressures of 3,4-, 5,6-, and 7,8-benzoquinoline are, respectively: combustion in the solid phase at 25°C, $\Delta H_c°$(c), −1565.67 ± 0.88, −1566.08 ± 1.49, and −1565.85 ± 0.95 kcal mol^{-1}; sublimation at a mean temperature of 35°C, $\Delta H_S°$(c), 22.60 ± 0.90, 19.86 ± 0.86, and 19.32 ± 0.61 kcal mol^{-1}; smoothed vapor pressures P in torr in the equation $\log P = A/T + B$, where T is the temperature in Kelvins, A = −4938 ± 199, −4340 ± 188, and −4222 ± 133; and B = 11.88 ± 0.65, 10.26 ± 0.62, and 10.50 ± 0.43. By use of appropriate auxiliary data, the enthalpies of formation in the gas phase, $\Delta H_f°$(g), are 58.19 ± 1.32, 55.86 ± 1.77, and 55.09 ± 1.20 kcal mol^{-1}; and the enthalpies of atomization in the gas phase, $\Delta H_a°$(g), are 2750.48 ± 1.95, 2752.81 ± 2.28, and 2753.58 ± 1.87 kcal mol^{-1}. The enthalpies of atomization are compared with reported values calculated by a semiempirical quantum mechanical SCF-CNDO procedure.

Carbon-nitrogen bond energies and resonance energies of conjugated aromatic and nonaromatic nitrogen-containing organic molecules continue to be uncertain because of a lack of gas-phase thermochemical data for such compounds. As part of a continuing study of the thermochemistry of nitrogen heterocyclics, we have measured the previously unreported enthalpies of combustion and sublimation of 3,4-, 5,6-, and 7,8-benzoquinoline, for which structural formulas are shown in Figure 1.

Experimental

Apparatus and procedure. The enthalpies of combustion were measured in a Parr Instrument Co. Series 1230 static oxygen bomb calorimeter operated adiabatically. Internal volume of the double-valve bomb, initially filled with oxygen at 30 atm, was 355 ml. Combustible impurities in the commercially available oxygen were removed by passing it slowly through copper oxide at 500°C and then through an activated molecular sieve to dry it. Temperature rise of the calorimeter was measured with a Leeds and Northrup type 8163-B platinum resistance thermometer. The resistance was measured with a Leeds and Northup 8060-B Mueller Bridge in conjunction with a null detector consisting of a Leeds and Northrup 9835-B DC microvolt amplifier and a Leeds and Northrup Speedomax G recorder. The calorimeter bucket water was weighed with a Griffin and George 5-kg balance with a precision of 20 mg division^{-1}.

Calibration of the calorimeter was by means of Parr Instrument Co. calorimetric grade benzoic acid with an enthalpy of combustion, certified by Parr on the basis of comparison with NBS Standard Reference benzoic acid, of 6317.83 cal g^{-1}. Five calibration runs gave a calorimetric equivalent of 2424.19 ± 0.38 cal K^{-1}. [Throughout this paper, cal = 4.184 J; torr = (101.325/760) kPa.]

Ignition for both calibration and experimental runs was accomplished with Parr iron alloy fuse wire weighed before and after combustion to establish the heat correction for slight oxidation of the wire. The weights of the pelleted samples of the benzoquinolines and benzoic acid were corrected to vacuum. Ten grams of water was used in the bomb, and the samples were burned without auxiliary material. The combustion gases were tested for the presence of carbon monoxide with Drager Co. gas detection tubes, type CO 10/a, which could detect a minimum of 0.4 ppm CO, and the inside of the bomb was carefully examined for soot. No carbon monoxide or unburned carbon was detected. The bomb washings were titrated with 0.1*N* NaOH to determine the correction for nitric acid formation. The results obtained were corrected to standard states by use of the Washburn corrections (2).

The vapor pressure and sublimation enthalpy experiments were carried out in a previously designed restricted molecular flow apparatus (5). The vapor pressures are given by

$$P = 17.14\frac{f}{\alpha}\frac{w}{\theta A}\left[\frac{T}{M}\right]^{1/2} \qquad (1)$$

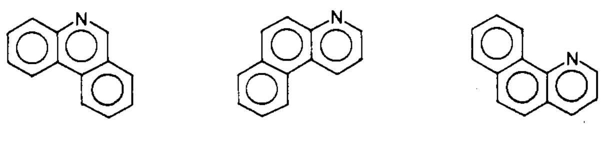
where P is the vapor pressure in torr, f is the apparatus restriction factor which is unitless, α is the evaporation coefficient which is unitless, w is the weight of substance sublimed in grams, θ is the duration of the sublimation run in sec, A is the surface area of the substance in cm^2, T is the temperature of the substance in Kelvins, and M is the molecular weight of the substance in g-mol^{-1}.

The enthalpy and entropy of sublimation were calculated from the temperature variation of the vapor pressure by a least-squares computer program (4) using the equation

$$\log P = \frac{-\Delta H_S°}{2.303\,R}\frac{1}{T} + \frac{\Delta S_S°}{2.303\,R} \qquad (2)$$

where $\Delta H_S°$ is the enthalpy of sublimation in cal mol^{-1}, $\Delta S_S°$ is the entropy of sublimation to 1 torr in cal K^{-1} mol^{-1}, and R is the gas constant in cal mol^{-1} K^{-1}.

Materials. The three benzoquinolines (Aldrich Chemical Co. purissimum and research grade) were purified by recrystallizing twice from aqueous ethanol, followed by drying over P_2O_5 in an Abderhalden drying pistol. They were kept in a dessicator over Drierite until combustion. The purities, determined by differential scanning calorimetry on a Perkin-Elmer DSC-1B instrument by the usual method (7), were 99.85, 99.87, and 99.00 mol % for 3,4-, 5,6-, and 7,8-benzoquinoline, respectively.



3,4-Benzoquinoline 5,6-Benzoquinoline 7,8-Benzoquinoline

Figure 1. Structures of compounds

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Table I. Summary of Combustion Experiments[a]

			3,4-Benzoquinoline				
m (compd), g	0.77412	0.75166	0.74258	0.75207	0.74560	0.74088	0.74524
Δt_c, deg	2.78593	2.70637	2.67279	2.70555	2.68113	2.66720	2.68438
n^i (H_2O), mol	0.5534	0.5534	0.5534	0.5534	0.5534	0.5534	0.5534
ϵ (calor) ($-\Delta t_c$), cal	−6753.62	−6560.76	−6479.35	−6558.77	−6499.57	−6465.80	−6507.45
ϵ (cont) ($-\Delta t_c$), cal	−40.04	−38.86	−38.30	−38.81	−38.51	−38.27	−38.48
ΔE, cor. to std. states, cal	7.65	7.42	7.31	7.43	7.36	7.28	7.34
ΔE^f, dec (HNO_3), cal	9.43	9.30	9.99	9.29	8.73	9.29	9.15
ΔE, ign, cal	18.97	18.09	18.90	16.94	17.36	18.58	19.35
$\Delta E_c^\circ/M$, cal g^{-1}	−8729.41	−8733.75	−8728.28	−8727.80	−8724.02	−8731.40	−8735.56
ΔE_c°, kcal mol^{-1}	−1564.51	−1565.29	−1564.31	−1564.23	−1563.55	−1564.87	−1565.62
Av and error interval, $\Delta E_c^\circ/M$, cal g^{-1}			−8730.03 ± 4.89				
Av and error interval, ΔE_c°, kcal mol^{-1}			−1564.63 ± 0.88				
			5,6-Benzoquinoline				
m (compd), g	0.74068	0.74200	0.73353	0.73769	0.71959		
Δt_c, deg	2.66732	2.66885	2.63990	2.65611	2.59379		
n^i (H_2O), mol	0.5534	0.5534	0.5534	0.5534	0.5534		
ϵ (calor) ($-\Delta t_c$), cal	−6466.09	−6469.80	−6399.62	−6438.92	−6287.84		
ϵ (cont) ($-\Delta t_c$), cal	−38.28	−38.15	−37.86	−38.10	−37.16		
ΔE cor. to std. states, cal	6.41	7.30	7.24	7.32	7.11		
ΔE^f, dec (HNO_3), cal	9.29	8.16	10.13	9.29	9.71		
ΔE, ign, cal	16.79	19.60	19.04	19.07	17.36		
$\Delta E_c^\circ/M$, cal g^{-1}	−8737.75	−8723.57	−8726.39	−8731.77	−8742.23		
ΔE_c°, kcal mol^{-1}	−1566.01	−1563.47	−1563.97	−1564.94	−1566.81		
Av and error interval, $\Delta E_c^\circ/M$, cal g^{-1}			−8732.34 ± 8.31				
Av and error interval, ΔE_c°, kcal mol^{-1}			−1565.04 ± 1.49				
			7,8-Benzoquinoline				
m (compd), g	0.75355	0.76089	0.74357	0.74989	0.74235	0.74966	
Δt_c, deg	2.71023	2.73803	2.67597	2.70120	2.67335	2.69838	
n^i (H_2O), mol	0.5534	0.5534	0.5534	0.5534	0.5534	0.5534	
ϵ (calor) ($-\Delta t_c$), cal	−6570.11	−6637.50	−6487.06	−6548.22	−6480.71	−6541.39	
ϵ (cont) ($-\Delta t_c$), cal	−38.95	−39.34	−38.41	−38.74	−38.15	−38.72	
ΔE, cor. to std. states, cal	7.45	7.52	7.33	7.40	7.32	7.42	
ΔE^f, dec (HNO_3), cal	10.41	10.27	10.69	10.27	9.85	9.85	
ΔE, ign, cal	16.52	15.65	16.90	16.76	19.63	16.91	
$\Delta E_c^\circ/M$, cal g^{-1}	−8724.94	−8731.09	−8728.90	−8737.99	−8731.81	−8731.87	
ΔE_c°, kcal mol^{-1}	−1563.71	−1564.82	−1564.42	−1566.05	−1564.94	−1564.95	
Av and error interval, $\Delta E_c^\circ/M$, cal g^{-1}			−8731.10 ± 5.31				
Av and error interval, ΔE_c°, kcal mol^{-1}			−1564.81 ± 0.95				

[a] Symbols and terminology are those of ref. 2, and errors were calculated according to ref. 6.

Table II. Summary of Sublimation Experiments

Temp, K	Time, θ, sec	Wt loss, W, g	Vp, P, torr
	3,4-Benzoquinoline		
			(Torr × 10^6)
288.26	43200	0.0022	6.3
293.10	25200	0.0021	10.4
298.20	18000	0.0030	21.0
303.13	18000	0.0056	39.5
308.23	14400	0.0092	81.8
313.17	10800	0.0105	125.4
318.24	7200	0.0135	243.9
323.15	4920	0.0156	415.6
	5,6-Benzoquinoline		
			(Torr × 10^5)
288.26	29400	0.0090	1.6
293.10	25200	0.0118	2.5
298.20	18000	0.0183	5.6
303.13	19800	0.0311	8.7
	5,6-Benzoquinoline		
			(Torr × 10^5)
308.23	14400	0.0386	14.9
313.17	3600	0.0156	24.3
318.24	3600	0.0268	42.0
323.15	3600	0.0428	67.6
	7,8-Benzoquinoline		
			(Torr × 10^4)
293.10	21600	0.0481	1.2
298.20	19200	0.0797	2.3
303.13	18000	0.1275	3.9
308.23	7140	0.0823	6.4
313.17	4200	0.0801	10.7
318.24	3600	0.1055	16.5
323.15	1800	0.0877	27.7

Table III. Enthalpy and Entropy of Sublimation

	$\Delta H_s°$, kcal mol^{-1}	$\Delta S_s°$, cal K^{-1} mol^{-1}
3,4-Benzoquinoline	22.60 ± 0.90	54.36 ± 3.94
5,6-Benzoquinoline	19.86 ± 0.86	46.93 ± 3.92
7,8-Benzoquinoline	19.32 ± 0.61	48.06 ± 2.73

Table IV. Combined Results

	Kcal mol^{-1}					
	$-\Delta H_c°$(c)	$\Delta H_s°$(c)	$-\Delta H_c°$(g)	$\Delta H_f°$(g)	$\Delta H_a°$	$\Delta H_a°$[a]
3,4-Benzoquinoline	1565.67 ± 0.88	22.60 ± 0.90	1588.27 ± 1.26	58.19 ± 1.32	2750.48 ± 1.95	2754.11 ± 1.71
5,6-Benzoquinoline	1566.08 ± 1.49	19.86 ± 0.86	1585.94 ± 1.72	55.86 ± 1.77	2752.81 ± 2.28	2754.60 ± 1.85
7,8-Benzoquinoline	1565.85 ± 0.95	19.32 ± 0.61	1585.17 ± 1.13	55.09 ± 1.20	2753.58 ± 1.87	2754.60 ± 1.85

[a] From ref. *1*.

Results

Combustion. The combustion data and results are summarized in Table I. These results are for the standard state reaction at 298.15K:

$$C_{13}H_9N(c) + \frac{61}{4}O_2(g) \rightarrow 13CO_2(g) + \frac{9}{2}H_2O(l) + \frac{1}{2}N_2(g)$$

The error intervals were calculated following the procedure of ref. *6*.

Sublimation. The data and results of the vapor-pressure measurements are presented in Tables II and III. The vapor pressures in Table II were calculated by using Equation 1 with $\alpha = 1$, $A = 2.54$ cm^2, and $f = 14.49$ for 3,4-benzoquinoline and $\alpha = 1$, $A = 3.64$ cm^2, and $f = 8.99$ for 5,6- and 7,8-benzoquinoline. In Table III the enthalpy and entropy of sublimation were calculated from Equation 2 at a 95% level of confidence (*4*), using the results of Table II.

Combined results. The enthalpies of formation, $\Delta H_f°$(g), and atomization, $\Delta H_a°$, in the gas phase of 3,4-, 5,6-, and 7,8-benzoquinoline were calculated from the results of Tables I and III using auxiliary data (*3*). The enthalpies of sublimation, valid at 35°C, were not corrected to 25°C since the heat capacity data are unavailable. Because of the small temperature interval, this introduces negligible error. The final values are shown in Table IV, together with values calculated using an SCF-CNDO quantum mechanical procedure (*1*). To facilitate comparison, the values of ref. *1* have been corrected to agree with recent values (*3*) for the enthalpies of atomization of the gaseous elements in their standard states.

Agreement between the experimental and theoretical enthalpies of atomization is within the quoted error limits for all three compounds. However, the data of Tables III and IV suggest that the slightly poorer agreement for 3,4-benzoquinoline could be due to a systematic error of about +1.5 cal mol^{-1} in its enthalpy of sublimation. Although a second series of vapor-pressure measurements for this compound confirmed the reported value, the possibility of this error being due to a small amount of impurity can only be ruled out by measurement of a sample purified by a different method and to a higher degree than used here.

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