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HEATS OF ATOMIZATION AND RESONANCE ENERGY OF SOME *ORTHO*-SUBSTITUTED BENZOIC ACIDS

MACK R. HOLDINESS

Department of Pharmacology and Experimental Therapeutics, Louisiana State University Medical Center, New Orleans, LA 70112 (U.S.A.)

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ABSTRACT

An experimental determination of heats of atomization of some *ortho*-substituted benzoic acids has been performed by combustion and differential scanning calorimetry. Resonance energy was calculated by the difference between the heat of atomization in the gas phase and the sum of the bond energies of a fixed bond structure for a resonating molecule. As the van der Waals radii of the *ortho*-substituent increased a decrease in resonance energy was observed.

INTRODUCTION

The resonance energy (RE) of a molecule can be defined as the energy difference between the most stable valence bond structure as determined by the sum of bond enthalpies and the energy of the actual molecule where the latter is the heat of atomization. In the treatment of a substance with the general molecular formula $C_aH_bO_cX_d$, the heat of atomization, $\Delta H^0_{f,a}$, of such a substance is illustrated by eqn. (1)

$$C_aH_bO_cX_d\,\{\text{solid}\} \rightarrow a\,C\{\text{gas}\} + b\,H\{\text{gas}\} + c\,O\{\text{gas}\} + d\,X\{\text{gas}\} + \Delta H^0_{f,a} \tag{1}$$

A reaction of this sort is not suitable for direct investigation, but the value of $\Delta H^0_{f,a}$ is obtained from the addition of a series of reactions which converts eqn. (1) to atomized components. If the bond dissociation reaction is carried out at 0 K, the bond energies are synonymous with bond enthalpies, $\Delta E^0_0 = \Delta H^0_0$. The calculations are conventionally based on enthalpies at 298 K; however, it should be noted that the difference between true bond energies and ΔH^0_{298} values is small, usually no more than one kcal mole^{-1}, and less than experimental thermochemical uncertainty.

Heats of hydrogenation are considered to be the most accurate thermochemical data available for RE measurement [1–3]; however, this data is not as extensive as might be desired. Heats of combustion are useful for RE

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determination since they are known for a large number of substances. Springall et al. [4] have utilized a procedure in calculating RE from bond energies and gas-phase atomization. With this method, the heat of combustion is experimentally determined and by employing the appropriate thermochemical equations the heat of atomization is calculated for the molecule. A stable valence bond Kekulé structure is drawn and from appropriate equations the total bond energy can be derived. The RE is found from eqn. (2)

$$\mathrm{RE} = \Delta H^0_{f,a} - \Sigma \bar{E}_b \tag{2}$$

where $\Delta H^0_{f,a}$ is the ΔH^0_{298} term for gas-phase atomization and $\Sigma \bar{E}_b$ is the sum of the average bond energy for all bonds of the molecule in question [4].

In this paper the heats of combustion are found experimentally and the method of Springall et al. [4] employed for determination of heats of atomization and RE. Correction factors are applied in the calculation of combustion data for elimination of experimental errors observed during the combustion process.

EXPERIMENTAL

Materials

High purity grades of commercial samples of 1-naphthoic acid, 2-naphthoic acid, naphthalene, 2-bromobenzoic acid, 2-chlorobenzoic acid, 2-iodobenzoic acid, 2-methylbenzoic acid and 2-methoxybenzoic acid were purchased from Aldrich Chemical Company. Benzoic acid was obtained from the National Bureau of Standards (6318 cal g^{-1}). All compounds were purified by zone refining and purity checked by C,H,O, halogen analysis and high-performance liquid chromatography as previously described [5].

Instrumentation

A Perkin-Elmer DSC-1B was used for analysis of heats of sublimation at a heating rate of 8 K min^{-1} as previously described [6]. The combustion apparatus was an oxygen bomb calorimeter with a 500-ml interval volume oxygen bomb from Parr Instrument Company. The bomb was housed in a nickel-plated 2.5 l calorimeter containing 2000 ml of distilled water. The whole apparatus was housed in a room maintained at 22°C ± 0.05°C. Water inside the calorimeter was stirred mechanically and its temperature monitored with a Beckman thermometer to within ±0.001°C.

Procedure

The water equivalent of the calorimeter was determined by burning pure benzoic acid. A weighed pellet of benzoic acid (1.0000 ± 0.0020 g) was placed in a brass crucible with 1 ml of water in the bomb. The bomb was flushed twice with 15 atm of high purity oxygen ($>99.5\%$) and then filled to a final pressure of 25 ± 0.2 atm. Following placement of the bomb in the calorimeter, 2000 ± 1 ml of distilled water at 22°C was added. After stirring for approximately 1 h, steady-state temperature conditions were reached and the pellet ignited electrically (with platinum wire with a known calorie content per cm) and the calorimeter temperature recorded at 1-min intervals for the following 20 min. The bomb was removed and washed out with distilled water and any nitric acid formed during the combustion process was determined by titration with 0.0100 M sodium hydroxide. Unburnt carbon was found by weighing. All benzoic acid derivatives and related compounds were analyzed for their ΔH_c^0 by this procedure. The values used for correction for nitric acid formation and any unburnt carbon were 13,960 cal mole^{-1} (heat of formation of dilute nitric acid from water, nitrogen (g) and oxygen (g) [7,8]) and 7840 cal g^{-1} (ΔH_c^0 graphite [9]), respectively.

The ΔH_c^0 values are experimentally determined at a mean temperature of 298 K. A relationship (eqn. (3)) is established between the heat of a reaction at constant pressure (ΔH_c^0) and at constant volume (ΔE_{298}^0) and may be written as [10]

$$\Delta E_{298}^0 = \Delta H_c^0 - P\Delta V \tag{3}$$

in which the reaction occurs at a constant pressure and the ΔV term is the increase in volume of the system. Assuming that the gases formed behave ideally the $P\Delta V$ term may be replaced by nRT and the relationship above may be written as (eqn. (4))

$$\Delta H_c^0 = \Delta E_{298}^0 + nRT \tag{4}$$

Addition of the corrections for fuse wire, nitric acid and graphite formation are as indicated in eqn. (5)

$$\Delta H_c^0 = \left[\Delta E_{298}^0 + nRT\right] - \text{corrections}[\text{fuse} + \text{HNO}_3 - \text{carbon}] \tag{5}$$

and all values of ΔH_c^0 are reported in kcal mole^{-1}.

Molecular energetics

Following experimental determination of ΔH_c^0 for the compounds in this study eqns. (6)–(13) are used for calculation of $\Delta H_{f,a}^0$

$$\Delta H_{f,298}^0\{\text{CO}_2\ (\text{g})\} = -94.05 \text{ kcal mole}^{-1}\ [11] \tag{6}$$

$$\Delta H_{f,298}^0\{\text{H}_2\text{O}\ (\text{l})\} = -68.32 \text{ kcal mole}^{-1}\ [11] \tag{7}$$

$$\Delta H_{f,298}^0\{\text{C}\ (\text{g})\} \rightarrow \text{C (graphite)} = -170.90 \text{ kcal mole}^{-1}\ [12] \tag{8}$$

$$\Delta H_{f,298}^0\{\text{H}_2\ (\text{g})\} \rightarrow 2\ \text{H (g)} = +104.20 \text{ kcal mole}^{-1}\ [13] \tag{9}$$

$$\Delta H_{f,298}^0\{\text{Cl}_2\ (\text{g})\} \rightarrow 2\ \text{Cl (g)} = +58.00 \text{ kcal mole}^{-1}\ [14] \tag{10}$$

$$\Delta H^0_{f,298}\{I_c\ (\text{solid})\} \rightarrow 2\ I\ (g) = +51.00\ \text{kcal mole}^{-1}\ [14] \tag{11}$$

$$\Delta H^0_{f,298}\{O_2\ (g)\} \rightarrow 2\ O\ (g) = +118.40\ \text{kcal mole}^{-1}\ [14] \tag{12}$$

$$\Delta H^0_{f,298}\{Br_2\ (l)\} \rightarrow 2\ Br\ (g) = +16.20\ \text{kcal mole}^{-1}\ [15] \tag{13}$$

The average bond energies are derived from the total energy that must be supplied to break all of the bonds of a molecule. In arriving at this particular term, the Kekulé structure of the molecule in question is drawn and the energies that represent the types and numbers of bonds are added together. Equations (14)–(22) represent the bond energy values used in this study

$$\text{C–H} = 99.50\ \text{kcal mole}^{-1}\ [16] \tag{14}$$

$$\text{C–C} = 83.10\ \text{kcal mole}^{-1}\ [13] \tag{15}$$

$$\text{C=C} = 145.00\ \text{kcal mole}^{-1}\ [17] \tag{16}$$

$$\text{C–I} = 50.10\ \text{kcal mole}^{-1}\ [18] \tag{17}$$

$$\text{C–Cl} = 78.30\ \text{kcal mole}^{-1}\ [14] \tag{18}$$

$$\text{C–Br} = 66.00\ \text{kcal mole}^{-1}\ [14] \tag{19}$$

$$\text{C=O} = 173.00\ \text{kcal mole}^{-1}\ [19] \tag{20}$$

$$\text{C–O} = 84.00\ \text{kcal mole}^{-1}\ [19] \tag{21}$$

$$\text{O–H} = 110.60\ \text{kcal mole}^{-1}\ [18] \tag{22}$$

These values were estimated from methane, ethane, ethylene, iodomethane, chloromethane, bromomethane, methanal, dimethylether and methanol, respectively. Equation (2) is used for the calculation of the RE of all the compounds studied.

RESULTS AND DISCUSSION

In Table 1 the ΔH^0_c of the nine compounds used in the study are listed. In most cases the correction factors for fuse, nitric acid and graphite formation did not significantly affect the experimentally determined ΔH^0_c values by more than ± 0.20 kcal mole^{-1}. Oxygen bomb samples, in which the correction factor for nitric acid is > 10 cal mole^{-1}, are usually found to be contaminated with the sample organic acid when analyzed by HPLC [5]. Any known literature values of ΔH^0_c for these compounds are listed in this table. As can be seen from this data there is excellent agreement ($\pm 3\%$ C.V.) between the literature and the ΔH^0_c obtained by this experimental method. Also listed in Table 1 are the previously determined heats of sublimation values which are used for calculation of the heats of atomization [6]. Table 2 presents a sample calculation of the $\Delta H^0_{f,a}$, $\Sigma \bar{E}_b$ and RE of benzoic acid. In Table 3 are presented the values of $\Delta H^0_{f,a}$, $\Sigma \bar{E}_b$, RE and van der Waals radii

TABLE 1

Heats of combustion [ΔH_c^0] and sublimation [ΔH_{sub}^0] [a]

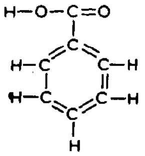
Compound	$-\Delta H_c^0$	Literature values $-\Delta H_c^0$[15]	ΔH_{sub}^0 [8]
Benzoic acid	770.20 ± 1.01	771.24	21.40 ± 0.10
2-Methylbenzoic acid	926.00 ± 1.11	928.90	32.90 ± 0.12
2-Methoxybenzoic acid	909.88 ± 1.60		21.90 ± 0.10
2-Chlorobenzoic acid	734.50 ± 1.09	734.50	27.77 ± 0.15
2-Bromobenzoic acid	737.30 ± 1.00		19.92 ± 0.10
2-Iodobenzoic acid	771.70 ± 1.71		24.61 ± 0.10
Naphthalene	1231.81 ± 1.23	1231.80	17.35 ± 0.10
1-Naphthoic acid	1231.10 ± 1.61	1231.80	28.10 ± 0.10
2-Naphthoic acid	1228.00 ± 1.72	1227.61	28.55 ± 0.14

[a] All values reported in kcal mole^{-1}.

TABLE 2

Sample calculation of the heats of atomization, average bond energy and resonance energy of benzoic acid [a]

$C_7H_6O_2$ (s) + 7.5 O_2 (g) → 7 CO_2 (g) + 3 H_2O (l)	$\Delta H_c^0 = -770.20$
$C_7H_6O_2$ (g) → $C_7H_6O_2$ (s)	$\Delta H_{sub}^0 = -21.00$
7 CO_2 (g) → 7 O_2 (g) + 7 C (graphite)	$\Delta H_f^0 = +658.35$
3 H_2O (l) → 1.5 O_2 (g) + 3 H_2 (g)	$\Delta H_f^0 = +204.96$
7 C (graphite) → 7 C (atoms)	$\Delta H_{f,a}^0 = +1196.30$
3 H_2 (g) → 6 H (atoms)	$\Delta H_{f,a}^0 = +312.60$
O_2 (g) → 2 O (atoms)	$\Delta H_{f,a}^0 = +118.40$
$C_7H_6O_2$ (g) → 7 C (atoms) + 6 H (atoms) + 2 O (atoms)	$\Delta H_{f,a}^0 = +1699.01$



Bond type	Number	Bond energy	Value *
C=C	3	145.00 =	435.00
C-C	4	83.10 =	332.40
C-H	5	99.50 =	497.50
C=O	1	173.00 =	173.00
C-O	1	84.00 =	84.00
O-H	1	110.60 =	110.60
		$\Sigma \bar{E}_b$ =	+1632.50

$\mathrm{RE} = \Delta H_{f,a}^0 - \Sigma \bar{E}_b = 1699.01 - 1632.50 = \underline{66.51}$

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[a] All values reported in kcal mole^{-1}.

TABLE 3

Heats of atomization, bond energies, resonance energies and van der Waals radii

Compound	$\Delta H^0_{f,a}$	$\Sigma \bar{E}_b$	RE	van der Waals radii (Å) [19]
Benzoic acid	1699.01	1632.50	66.51	
2-Methylbenzoic acid	1969.18	1914.60	54.58	1.72
2-Methoxybenzoic acid	2055.50	1999.50	56.00	1.80
2-Chlorobenzoic acid	1671.08	1611.30	59.78	1.77
2-Bromobenzoic acid	1655.23	1599.00	56.23	1.92
2-Iodobenzoic acid	1633.54	1583.10	50.44	2.06
Naphthalene	2090.43	2019.60	70.83	
1-Naphthoic acid	2463.73	2370.80	92.93	
2-Naphthoic acid	2467.23	2370.80	96.43	

of the *ortho*-substituent [19]. As can be observed from this data, as the size of the *ortho*-substituent increases, the RE of the corresponding acid decreases. Ferguson [20] has discussed the theory that atoms involved in resonance structure must be coplanar for maximum RE. Often spatial requirements prevent such coplanarity and, accordingly, it is found that resonance is decreased or inhibited. In aromatic systems this is primarily interpreted to be a steric effect; for *ortho*-substituted benzoic acids, the substituent may force the carboxyl group out of the plane of the ring, thereby decreasing the resonance of the system [18]. As might be expected and as demonstrated in this paper the larger the substituent the greater the decrease in RE of the molecule in question.

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