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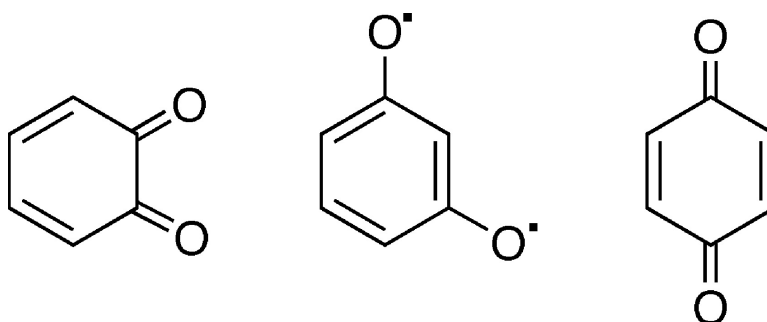
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# The Enthalpies of Formation of *o*-, *m*-, and *p*-Benzoquinone: Gas-Phase Ion Energetics, Combustion Calorimetry, and Quantum Chemical Computations Combined

Alireza Fattahi,<sup>†</sup> Steven R. Kass,<sup>\*,†</sup> Joel F. Liebman,<sup>\*,‡</sup> M. Agostinha R. Matos,<sup>\*,§</sup> Margarida S. Miranda,<sup>§</sup> and Victor M. F. Morais<sup>§,||</sup>

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**Abstract:** Radical anions of *o*-, *m*-, and *p*-benzoquinone were produced in a Fourier transform mass spectrometer by low energy electron attachment or collision-induced dissociation and were differentiated. Classical derivatization experiments also were carried out to authenticate the ortho and meta anions. Gas-phase techniques were used to measure the proton affinities of all three radical anions and the electron affinities of *o*- and *m*-benzoquinone. By combining these results in thermodynamic cycles, we derived heats of hydrogenation of *o*-, *m*-, and *p*-benzoquinone ( $\Delta_{\text{hyd}}H^\circ(\mathbf{1o}, \mathbf{1m}, \text{and } \mathbf{1p}) = 42.8 \pm 4.1, 74.8 \pm 4.1, \text{ and } 38.5 \pm 3.0 \text{ kcal mol}^{-1}$ , respectively) and their heats of formation ( $\Delta_f H^\circ(\mathbf{1o}, \mathbf{1m}, \text{and } \mathbf{1p}) = -23.1 \pm 4.1, 6.8 \pm 4.1, \text{ and } -27.7 \pm 3.0 \text{ kcal mol}^{-1}$ , respectively). Good accord with the literature value for the para derivative was obtained. Combustion calorimetry and heats of sublimation also were measured for benzil and 3,5-di-*tert*-butyl-*o*-benzoquinone. The former heat of formation agreed with previous determinations, while the latter result ( $\Delta_f H^\circ(\text{g}) = -73.09 \pm 0.87 \text{ kcal mol}^{-1}$ ) was transformed to  $\Delta_f H^\circ(\mathbf{1o}) = -18.9 \pm 2.2 \text{ kcal mol}^{-1}$  by removing the effect of the *tert*-butyl groups via isodesmic reactions. This led to a final value of  $\Delta_f H^\circ(\mathbf{1o}) = -21.0 \pm 3.1 \text{ kcal mol}^{-1}$ . Additivity was found to work well for *m*-benzoquinone, but BDE1 and BDE2 for 1,2- and 1,4-dihydroxybenzene differed by a remarkably small  $14.1 \pm 4.2$  and  $23.5 \pm 3.7 \text{ kcal mol}^{-1}$ , respectively, indicating that *o*- and *p*-benzoquinone should be excellent radical traps.

## Introduction

Quinones are naturally occurring and widely found compounds that have been known since antiquity as pigments and medicines.<sup>1–4</sup> *p*-Benzoquinone (**1p**) was first prepared some 170 years ago in the earliest era of chemical synthesis, and since then a rich chemistry involving complexes, oxidation–reduction reactions, photochemical processes, polymeric materials, synthetic transformations, and biochemical redox transformations in crucial events such as photosynthesis and respiration has been uncovered or developed.

Two isomeric forms of quinones are commonly encountered (ortho and para), but the meta isomer also is of interest and has been the subject of extensive discussions since it formally is

missing a bond and is an avatar of the so-called non-Kekulé species (Chart 1).<sup>5,6</sup> Of these quinone compounds, only the *p*-isomer has a measured heat of formation, and its value is well-established ( $\Delta_f H^\circ(\text{g}) = -29.3 \pm 0.9 \text{ kcal mol}^{-1}$ ).<sup>7</sup> No literature reports on the enthalpy of formation of *o*- and *m*-benzoquinone (**1o** and **1m**) or any of their substituted derivatives have appeared despite extensive efforts to fully characterize these species. In this study, the enthalpies of formation of *o*-, *m*-, and *p*-benzoquinone were determined by carrying out gas-phase ion energetic measurements, combustion calorimetry and phase-change determinations, and high-level quantum chemical computations.

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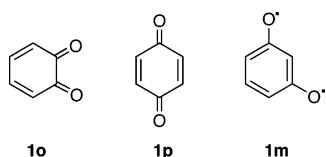
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Chart 1



## Experimental Section

***o*-Benzoquinone (1o).** This compound was prepared by a modification of Fischer and Henderson's previously reported procedure.<sup>8</sup> That is, a well-stirred solution of 0.11 g (1.0 mmol) of catechol (1,2-dihydroxybenzene) and 3 g of anhydrous magnesium sulfate in 10 mL of dry ether was cooled to 0 °C. Cerium (IV) on silica gel (6.94 g, 2.1 mmol)<sup>8</sup> was added, and the mixture was shaken for exactly 3 min. It was then rapidly suction-filtered through a jacketed funnel and cooled to -78 °C. The residue was washed with 20 mL of cold ether and combined with the filtrate. Concentration of the solution at -25 °C under reduced pressure to a volume of ~3 mL was followed by crystallization at -78 °C to give 90 mg (83%) of the red product. This quinone can be kept unchanged for two months by storing it in the dark at -78 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.43 (m, 2H), 7.06 (m, 2H).

**Ion Energetics.** Gas-phase experiments were carried out with a dual cell model 2001 Finnigan Fourier transform mass spectrometer (FTMS) equipped with a 3 T superconducting magnet and controlled by a Sun workstation running the Odyssey software 4.2 package or a similar instrument which is controlled by an Ion Spec data system running IonSpec99 ver. 7.0. *ortho*-Benzoquinone and *para*-benzoquinone radical anions were generated by electron attachment using low energy electrons (3.5 eV), and the meta isomer was prepared from *m*-nitrophenoxide (which was made by reacting the trimethylsilyl ether of *m*-nitrophenol with fluoride ion) by collision-induced dissociation (CID) as previously reported.<sup>9</sup> The desired *m/z* 108 ions were isolated using stored-waveform inverse Fourier transform (SWIFT)<sup>10</sup> excitations and then were transferred to the second (source) cell where they were translationally and vibrationally cooled with a pulse of argon up to a pressure of ~1 × 10<sup>-5</sup> Torr. Neutral reagents were added to the source cell via slow leak valves or a solid inlet probe, and all of the resulting reactions were monitored as a function of time. For the electron affinity bracketing experiments it was particularly important to use low pressures (~1 × 10<sup>-8</sup> Torr) of the reference compounds to minimize adventitious electron capture from stray electrons. This process was monitored by double resonance (i.e., by continually ejecting the *m/z* 108 ion and observing the effect on electron transfer) as well as by running the reactions without transferring the ion of interest to the source cell.

To confirm the structure of the *o*-benzoquinone radical anion, it was converted to the conjugate base of catechol by reaction with *tert*-butyl mercaptan using sustained off-resonance irradiation (SORI)<sup>11</sup> to drive the process. The resulting hydrogen-atom transfer product was bracketed with standard reference acids and further characterized by CID. These results were compared to the authentic conjugate base of catechol, which was generated by deprotonating 1,2-dihydroxybenzene with OH<sup>-</sup>; hydroxide ion was made by electron ionization of H<sub>2</sub>O at 9 eV. We also converted the meta isomer to its nitrite (C<sub>6</sub>H<sub>4</sub>(ONO)O<sup>-</sup>) by addition of nitric oxide to **2m**, and the resulting species was characterized by CID and bracketing its proton affinity.

**Computations.** Calculations were carried out using the U.K. version of GAMESS<sup>12,13</sup> and Gaussian 2003<sup>14</sup> on IBM and SGI workstations. G3 theory was employed for the parent quinones (**1o** and **1p**) and related species.<sup>15</sup> The larger *tert*-butyl substituted compounds were optimized

using the Becke three-parameter hybrid exchange<sup>16</sup> and Lee–Yang–Parr<sup>17</sup> correlation density functional (B3LYP) and the 6-31G(d) and 6-31+G(d) basis sets. B3LYP single-point energies were obtained with the 6-311G(d,p) and 6-311+G(2df,2pd)<sup>18</sup> basis sets, and all of the resulting energetic quantities include zero-point energies and have been adjusted to 298.15 K, except for electron affinities which are at 0 K. Unscaled vibrational frequencies were used for the density functional theory (DFT) calculations, whereas the Hartree–Fock frequencies were scaled by 0.8929 as called for in the G3 procedure. However, HF frequencies can lead to significant errors in zero-point energies and temperature corrections; thus, G3 results with DFT frequencies also are given, and they are provided in parentheses.

## Combustion Calorimetry

**Materials and Purity Control.** 3,5-Di-*tert*-butyl-*o*-benzoquinone and benzil (PhCOCOPh) were obtained commercially from Aldrich with mass fraction purities of 0.993 and 0.9980, respectively, as determined by gas–liquid chromatography. These compounds were further purified by repeated vacuum sublimations before the calorimetric measurements. Their purity was assessed by differential scanning calorimetry (Setaram DSC 141) via a fractional fusion technique.<sup>19</sup> The samples, hermetically sealed in stainless steel crucibles, were heated using a heating rate of 1.67 × 10<sup>-2</sup> K s<sup>-1</sup>, and the resulting thermograms did not show any phase transitions between *T* = 298 K and the melting temperature of the studied compounds. Three high-purity reference materials (naphthalene, benzoic acid, and indium)<sup>20</sup> were used to calibrate the temperature scale of the calorimeter, and its power scale was calibrated with high purity indium (mass fraction > 0.99999). Enthalpies of fusion of the crystalline compounds and their purity were derived from the DSC experiments and are presented in Table 1, where the uncertainties are twice the standard deviations of the mean of six independent runs.

Sample purities also were confirmed via carbon dioxide recovery ratios. In particular, the average ratios of the mass of

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**Table 1.** Temperatures of Fusion,  $T_{\text{fus}}$ , Enthalpies of Fusion,  $\Delta^1_{\text{cr}}H^\circ(T_{\text{fus}})$ , and Purity of the Studied Compounds

compound	$T_{\text{fus}}$ (K)	$\Delta^1_{\text{cr}}H^\circ(T_{\text{fus}})$ (kcal mol <sup>-1</sup> )	purity (%)
3,5-di- <i>tert</i> -butyl- <i>o</i> -benzoquinone	387.89 ± 0.08	6.341 ± 0.057	99.94 ± 0.01
benzil	368.13 ± 0.11	5.468 ± 0.047	99.93 ± 0.04

the recovered carbon dioxide to that calculated from the mass of sample, together with the standard deviation of the mean, were  $1.0003 \pm 0.0003$  (3,5-di-*tert*-butyl-*o*-benzoquinone) and  $1.0008 \pm 0.0001$  (benzil). The density of 3,5-di-*tert*-butyl-*o*-benzoquinone was estimated from the mass and the dimensions of the pellets that were used for the combustion experiments ( $\rho = 0.87 \text{ g cm}^{-3}$ ), while that for benzil was taken as  $\rho = 1.084 \text{ g cm}^{-3}$ .<sup>21</sup>

**Calorimetry.** Combustion experiments were performed with a static bomb calorimeter that previously has been described in detail.<sup>22,23</sup> Benzoic acid (Bureau of Analyzed Samples, Thermochemical Standard, BCS-CRM-190) was used to calibrate the bomb. Its measured energy of combustion is  $\Delta_{\text{cu}} = -6318.14 \pm 0.84 \text{ cal g}^{-1}$  under certificate conditions. The calibration results were corrected to give the energy equivalent  $\epsilon_{\text{cal}}$  corresponding to the average mass of water added to the calorimeter, 3119.6 g. From six calibration experiments,  $\epsilon_{\text{cal}} = 3825.29 \pm 0.48 \text{ cal K}^{-1}$ , where the uncertainty quoted is the standard deviation of the mean. For all experiments, crystalline samples in pellet form were ignited at  $T = 298.150 \pm 0.001 \text{ K}$  in oxygen at  $p = 3.04 \text{ MPa}$ , with  $1.00 \text{ cm}^3$  of water added to the bomb. The electrical energy for ignition  $\Delta U(\text{ign})$  was determined from the change in potential across a capacitor when it was discharged through the platinum ignition wire. Corrections for combustion of the cotton thread fuse, nitric acid formation, and carbon formation were made as previously described.<sup>24,25</sup> The mass of the compound,  $m(\text{compound})$ , used in each experiment was determined from the total mass of carbon dioxide,  $m(\text{CO}_2, \text{total})$ , produced after allowance for that formed from the cotton thread fuse. An estimated pressure coefficient of specific energy,  $(\partial u/\partial p)_T = -0.05 \text{ cal g}^{-1} \text{ MPa}^{-1}$  at  $T = 298.15 \text{ K}$ , a typical value for most organic compounds, was assumed.<sup>26</sup> The molar masses used for the elements were those recommended by the IUPAC commission.<sup>27</sup>

As samples were ignited at  $T = 298.15 \text{ K}$ ,

$$\Delta U(\text{IBP}) = -\{\epsilon_{\text{cal}} + \Delta m(\text{H}_2\text{O})c_p(\text{H}_2\text{O}, \text{l}) + \epsilon_f\}\Delta T_{\text{ad}} + \Delta U(\text{ign}) \quad (1)$$

where  $\Delta U(\text{IBP})$  is the energy associated with the isothermal bomb process,  $\epsilon_{\text{cal}}$  is the energy equivalent of the calorimeter without contents and corrected for the mass of water (3119.6

**Table 2.** Standard ( $p^\circ = 0.1 \text{ MPa}$ ) Molar Enthalpies of Combustion, Sublimation, and Formation at  $T = 298.15 \text{ K}$  in the Crystalline and Gaseous Phases

	3,5-di- <i>tert</i> -butyl- <i>o</i> -benzoquinone	benzil
$\Delta_{\text{cu}}U^\circ$ <sup>a</sup>	$-8619.84 \pm 0.72$	$-7696.29 \pm 1.17$
$\Delta_{\text{c}}U^\circ(\text{cr})^b$	$-1899.04 \pm 0.69$	$-1618.00 \pm 0.67$
$\Delta_{\text{c}}H^\circ(\text{cr})^b$	$-1901.41 \pm 0.69$	$-1618.88 \pm 0.67$
$\Delta_{\text{f}}H^\circ(\text{cr})^b$	$-98.45 \pm 0.81$	$-39.41 \pm 0.79$
$\Delta_{\text{cr}}H^\circ$ <sup>b</sup>	$25.36 \pm 0.31$	$25.41 \pm 0.67$
$\Delta_{\text{f}}H^\circ(\text{g})^b$	$-73.09 \pm 0.87$	$-14.0 \pm 1.0$

<sup>a</sup> In cal g<sup>-1</sup>. <sup>b</sup> In kcal mol<sup>-1</sup>.

g),  $\Delta m(\text{H}_2\text{O})$  is the difference of added water from the previously mentioned standard value,  $\epsilon_f$  is the energy of the bomb contents after ignition,  $\Delta T_{\text{ad}}$  is the adiabatic temperature rise (the calorimeter temperature change corrected for heat exchange and the work of stirring), and  $\Delta U(\text{ign})$  is the energy of ignition. For each compound, the standard measured energy of combustion,  $\Delta_{\text{cu}}U^\circ$ , was calculated by the procedure given by Hubbard et al.<sup>28</sup> The mean values of  $\Delta_{\text{cu}}U^\circ$  were derived from 10 independent experiments for 3,5-di-*tert*-butyl-*o*-benzoquinone and from six experiments for benzil. These values and the corresponding uncertainties (calculated as the standard deviation of the mean) are given for each compound in Table 2. The derived standard molar energies and enthalpies of combustion,  $\Delta_{\text{c}}U^\circ(\text{cr})$  and  $\Delta_{\text{c}}H^\circ(\text{cr})$ , and the standard molar enthalpies of formation for the compounds in the crystalline phase,  $\Delta_{\text{f}}H^\circ(\text{cr})$ , at  $T = 298.15 \text{ K}$  are also provided in Table 2. In accordance with normal thermochemical practice,<sup>29</sup> the uncertainties assigned to the standard molar enthalpies of combustion are, in each case, twice the overall standard deviation of the mean and include the uncertainties in the calibration. To derive  $\Delta_{\text{f}}H^\circ(\text{cr})$  from  $\Delta_{\text{c}}H^\circ(\text{cr})$ , the standard molar enthalpies of formation of  $\text{H}_2\text{O}(\text{l})$  and  $\text{CO}_2(\text{g})$  at  $T = 298.15 \text{ K}$  found in the literature were used.<sup>30</sup>

**Microcalorimetry Calvet.** The standard molar enthalpies of sublimation were measured using the “vacuum sublimation” drop microcalorimetric method.<sup>31</sup> Samples of about 3–4 mg were placed in thin glass capillary tubes sealed at one end and were dropped at room temperature into the hot reaction vessel in a high-temperature Calvet microcalorimeter (SETARAM HT 1000) held at a convenient temperature  $T$ . They were then removed from the hot zone by vacuum sublimation. For these measurements, the microcalorimeter was calibrated in situ using the reported standard molar enthalpy of sublimation of naphthalene.<sup>32</sup> The observed enthalpies of sublimation were corrected to  $T = 298.15 \text{ K}$  using the equation

$$\Delta T_{298.15\text{K}}H^\circ(\text{g}) = \int_{298.15\text{K}}^T C_{\text{p,m}}^\circ(\text{g}) dT \quad (2)$$

where

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$$C_p^{\circ}(g) = 1.08 \times 10^{-4} T^2 + 0.264T + 0.0678 \quad (3)$$

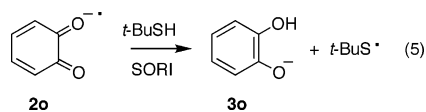
and

$$C_p^{\circ}(g) = -1.31 \times 10^{-4} T^2 + 0.250T - 11.6255 \quad (4)$$

are for 3,5-di-*tert*-butyl-*o*-benzoquinone and benzil, respectively. These equations were derived from statistical thermodynamics and calculated vibrational frequencies at the B3LYP/6-31G(d) level. The mean values of the standard molar enthalpy of sublimation ( $\Delta_{\text{cr}}^{\circ}H^{\circ}$ ) at  $T = 298.15$  K were obtained for 3,5-di-*tert*-butyl-*o*-benzoquinone and benzil from six and seven experiments, respectively (Table 2), and the assigned uncertainties represent twice the standard deviations of the mean. Combining the values of  $\Delta_f H^{\circ}(\text{cr})$  and  $\Delta_{\text{cr}}^{\circ}H^{\circ}$  for each compound, we obtained the standard molar enthalpies of formation in the gas phase ( $\Delta_f H^{\circ}(g)$ ); these are given in Table 2.

## Results and Discussion

**Ion Energetics. Structural Authentication.** Electron attachment of low energy electrons by *o*- and *p*-benzoquinone (**1o** and **1p**) affords the corresponding radical anions (**2o** and **2p**). These ions previously have been reported,<sup>9,33,34</sup> but we felt it was important, nevertheless, to establish the structure of the less stable species (**2o**). This was accomplished by reacting **2o** with *tert*-butyl mercaptan under conditions in which the ion is energized (i.e., SORI)<sup>11</sup> so as to drive a hydrogen-atom abstraction and afford the conjugate base of catechol (**3o**, eq 5).



The identity of this phenoxide ion was verified by bracketing its proton affinity, fragmenting it by CID, and comparing the results to the independently prepared ion made by deprotonating 1,2-dihydroxybenzene with  $\text{OH}^-$ . In particular, **3o** deprotonates chloroacetic acid ( $\Delta_{\text{acid}}^{\circ}H^{\circ} = 336.5 \pm 2.2$  kcal mol<sup>-1</sup>) but not trimethylacetic acid or acetic acid ( $\Delta_{\text{acid}}^{\circ}H^{\circ} = 344.7 \pm 2.1$  and  $348.6 \pm 2.9$  kcal mol<sup>-1</sup>, respectively), which is in accord with the literature proton affinity of  $339.6 \pm 2.1$  kcal mol<sup>-1</sup>.<sup>7</sup> Likewise, off-resonance CID leads to signal loss and shows the same energy dependence independently of how **3o** is produced.

*m*-Benzoquinone radical anion was readily differentiated from the ortho and para isomers (see below) and was converted to its corresponding nitrite upon reaction with nitric oxide. The resulting *m*-nitrosooxyphenoxide ( $\text{C}_6\text{H}_4(\text{ONO})\text{O}^-$ ) deprotonates chloroacetic acid but not 4-oxopentanoic acid, which enabled us to assign  $\Delta_{\text{acid}}^{\circ}H^{\circ} = 338.6 \pm 2.8$  kcal mol<sup>-1</sup>. This value is larger than the acidity of *m*-nitrophenol ( $334.4 \pm 2.1$  kcal mol<sup>-1</sup>) and is in excellent agreement with a computed B3LYP/6-311+G(2df,2pd)//B3LYP/6-31+G(d) value of  $338.4$  kcal mol<sup>-1</sup>; the computed value for the nitro derivative is  $332.9$  kcal mol<sup>-1</sup>. In both cases the larger basis set is needed to reproduce the experimental results, and the 6-31+G(d) acidities are numerically too small by  $\sim 6$  kcal mol<sup>-1</sup>. Collision-induced dissociation of the nitrosooxyphenoxide ion, interestingly, also is different from the nitrophenoxide in that the former ion leads exclusively

**Table 3.** Proton Affinity Bracketing Results for *o*-, *m*-, and *p*-Benzoquinone Radical Anions (**2o**, **2m**, and **2p**)

ref. acid (HX)	$\Delta_{\text{acid}}^{\circ}H^{\circ}$ (kcal mol <sup>-1</sup> ) <sup>a</sup>	proton transfer		
		<b>2o</b>	<b>2m</b>	<b>2p</b>
CH <sub>3</sub> CO <sub>2</sub> H	348.1 ± 2.2	—	no	no
(CH <sub>3</sub> ) <sub>3</sub> CCO <sub>2</sub> H	344.7 ± 2.1	no	no	—
CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CO <sub>2</sub> H	342.0 ± 2.0	—	no	—
CH <sub>3</sub> COCH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> H	340.7 ± 2.9	—	no	—
ClCH <sub>2</sub> CO <sub>2</sub> H	336.5 ± 2.2	no	yes	no
CF <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> H	333.9 ± 2.0	yes	—	no
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (NO <sub>2</sub> )CO <sub>2</sub> H	331.8 ± 2.2	—	—	no
NCCH <sub>2</sub> CO <sub>2</sub> H	330.3 ± 2.1	—	—	yes
Cl <sub>2</sub> CHCO <sub>2</sub> H	328.4 ± 2.1	yes	—	—
<i>p</i> -C <sub>6</sub> H <sub>4</sub> (NO <sub>2</sub> )CO <sub>2</sub> H	328.1 ± 2.2	—	—	yes
CF <sub>3</sub> CO <sub>2</sub> H	323.8 ± 2.9	—	—	yes

<sup>a</sup> Acidity values taken from ref. 7.

to NO<sub>2</sub><sup>-</sup>, whereas the latter species gives the radical anion of *m*-benzoquinone as well as NO<sub>2</sub><sup>-</sup>.

**Proton Affinities.** The proton affinities of **2o**, **2m**, and **2p** were determined by reacting these ions with standard reference acids and observing the occurrence or non-occurrence of proton transfer (Table 3). *o*-Benzoquinone radical anion undergoes proton transfer with CF<sub>3</sub>CH<sub>2</sub>CO<sub>2</sub>H and Cl<sub>2</sub>CHCO<sub>2</sub>H ( $\Delta_{\text{acid}}^{\circ}H^{\circ} = 333.9 \pm 2.0$  and  $328.4 \pm 2.1$  kcal mol<sup>-1</sup>, respectively), but not with weaker acids such as ClCH<sub>2</sub>CO<sub>2</sub>H and (CH<sub>3</sub>)<sub>3</sub>CCO<sub>2</sub>H ( $\Delta_{\text{acid}}^{\circ}H^{\circ} = 336.5 \pm 2.2$  and  $344.7 \pm 2.1$  kcal mol<sup>-1</sup>, respectively). The para ion is a weaker base and undergoes proton transfer with cyanoacetic acid, *p*-nitrobenzoic acid, and trifluoroacetic acid ( $\Delta_{\text{acid}}^{\circ}H^{\circ} = 330.3 \pm 2.1$ ,  $328.1 \pm 2.2$ , and  $323.8$  kcal mol<sup>-1</sup>, respectively) but not weaker acids such as *o*-nitrobenzoic acid and 3,3,3-trifluoropropionic acid ( $\Delta_{\text{acid}}^{\circ}H^{\circ} = 331.8 \pm 2.2$  and  $333.9 \pm 2.0$  kcal mol<sup>-1</sup>, respectively). *m*-Benzoquinone radical anion is the strongest base of the three isomers and undergoes proton transfer with chloroacetic acid but not with 4-oxopentanoic acid (CH<sub>3</sub>COCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H). These results enable us to assign PA(**2o**) =  $335.2 \pm 2.0$  kcal mol<sup>-1</sup>, PA(**2m**) =  $338.6 \pm 2.8$  kcal mol<sup>-1</sup>, and PA(**2p**) =  $331.1 \pm 1.7$  kcal mol<sup>-1</sup>, which are in reasonable accord with G3 theory results of  $336.9$  (335.5),  $335.6$  (337.4), and  $325.0$  (326.5) kcal mol<sup>-1</sup>, respectively; the parenthetical values were computed using unscaled B3LYP/6-31G(d) vibrational frequencies instead of the Hartree–Fock values.

**Electron Affinities.** The electron binding energies of **2o** and **2m** or equivalently the electron affinities of **1o** and **1m** were determined by bracketing. The ortho radical anion undergoes electron transfer upon reaction with 1,4-dinitrobenzene but not with 3,5-bis(trifluoromethyl)nitrobenzene and *p*-nitrobenzaldehyde, whereas the meta species reacts with titanium tetrachloride but not with tetrachloro-1,4-benzoquinone or reagents with lower electron affinities (Table 4). These results enable us to assign EA(**1o**) =  $1.90 \pm 0.13$  eV ( $43.8 \pm 3.0$  kcal mol<sup>-1</sup>) and EA(**1m**) =  $2.82 \pm 0.10$  eV ( $65.0 \pm 2.3$  kcal mol<sup>-1</sup>), which are in excellent accord with the predicted values of 2.00 (1.96) and 2.91 (2.88) eV using G3 theory, but the former quantity is significantly greater than the previously reported experimental value of  $1.620 \pm 0.048$  eV.<sup>33</sup> The same group also reported EA(**1p**) =  $1.990 \pm 0.048$  eV, which is significantly larger than a more recent determination of  $1.860 \pm 0.006$  eV<sup>34</sup> and does not agree quite as well with our G3 prediction of 1.91 (1.90) eV. In addition, the electron affinity of *o*-benzoquinone is computed to be 0.09 (0.06) eV larger than that for *p*-

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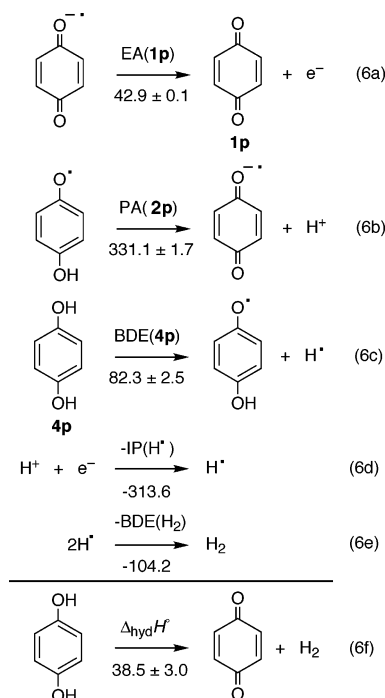
**Table 4.** Electron Affinity Bracketing Results for *o*- and *m*-Benzoquinone (**1o** and **1m**)

ref. compd	EA (eV) <sup>a</sup>	electron transfer	
		<b>1o</b>	<b>1m</b>
<i>p</i> -C <sub>6</sub> H <sub>4</sub> (NO <sub>2</sub> )CHO	1.69 ± 0.09	no	—
3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NO <sub>2</sub>	1.79 ± 0.10	no	—
<i>p</i> -C <sub>6</sub> H <sub>4</sub> (NO <sub>2</sub> ) <sub>2</sub>	2.00 ± 0.10	yes	no
trichloro- <i>p</i> -benzoquinone	2.611 ± 0.048	—	no
tetrachloro- <i>p</i> -benzoquinone	2.754 ± 0.048	—	no
TiCl <sub>4</sub>	2.88 ± 0.15	—	yes

<sup>a</sup> Values taken from ref 7.

benzoquinone, which is consistent with our value for the ortho compound and the more recent literature determination (0.04 ± 0.13 eV) but is in poor accord with the Brauman et al. difference of  $-0.37 \pm 0.07$ . Our difference in the electron affinities also is in excellent accord with the 0.077 eV difference in the measured liquid-phase reduction potentials.<sup>35</sup>

**Enthalpies of Formation.** The thermochemical data for *o*-, *m*-, and *p*-benzoquinone radical anions can be used to derive the enthalpies of hydrogenation of the corresponding neutral quinones and their enthalpies of formation. The former quantities can be derived by combining the electron and proton affinities of **1o**, **1m**, or **1p**, the bond dissociation energies of *o*-, *m*-, or *p*-dihydroxybenzene<sup>36</sup> and molecular hydrogen, and the ionization potential of hydrogen atom in a thermodynamic cycle as illustrated for *p*-benzoquinone (eq 6, all values are in kcal mol<sup>-1</sup>).

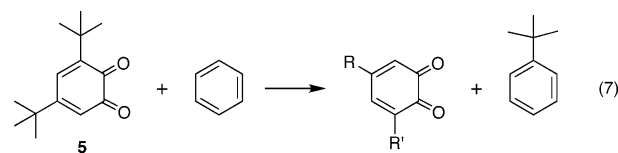


The resulting enthalpies of hydrogenation for *o*-, *m*-, and *p*-benzoquinone are  $42.8 \pm 4.1$ ,  $74.8 \pm 4.1$ , and  $38.5 \pm 3.0$  kcal mol<sup>-1</sup>, respectively. These values are in good agreement with the G3 predictions of 44.6 (45.7), 72.2 (73.4), and 34.1

(35.2) kcal mol<sup>-1</sup>, respectively.<sup>37</sup> The resulting enthalpies of formation ( $\Delta_f H^\circ$ (**1o**, **1m**, and **1p**) =  $-23.1 \pm 4.1$ ,  $6.8 \pm 4.1$ , and  $-27.7 \pm 3.0$  kcal mol<sup>-1</sup>) and their differences ( $4.6 \pm 5.1$  (**1o** - **1p**) and  $34.5 \pm 5.1$  (**1m** - **1p**) kcal mol<sup>-1</sup>) are in excellent agreement with the G3 enthalpies of formation ( $-19.7$  ( $-17.4$ ) (**1o**),  $8.4$  ( $10.5$ ) (**1m**), and  $-27.6$  ( $-25.5$ ) (**1p**) kcal mol<sup>-1</sup>) computed via atomization energies and the resulting energy differences of 7.9 (8.1) (**1o** - **1p**) and 36.0 (36.0) (**1m** - **1p**) kcal mol<sup>-1</sup>. It is also worth noting that the computed enthalpies of formation for *o*-, *m*-, and *p*-dihydroxybenzene ( $-64.3$  ( $-61.0$ ),  $-63.8$  ( $-60.5$ ), and  $-61.6$  ( $-58.5$ ) kcal mol<sup>-1</sup>) using the HF vibrational frequencies are in modest accord with the experimental values of  $-65.9 \pm 0.3$ ,  $-68.0 \pm 0.3$ , and  $-66.2 \pm 0.3$  kcal mol<sup>-1</sup> (Table 5).<sup>38</sup>

**Combustion Calorimetry.** Benzil was examined in a control experiment since it is a 14-carbon  $\alpha$ -diketone just like di-*tert*-butyl-*o*-benzoquinone (**5**) and its thermochemistry previously has been reported. Our measured standard molar enthalpy of formation in the solid phase is  $-39.41 \pm 0.79$  kcal mol<sup>-1</sup>, which is very nearly the average of the two most contemporaneous values in the literature (i.e.,  $-42.8 \pm 1.0$  and  $-36.8 \pm 1.0$  kcal mol<sup>-1</sup>).<sup>39,40</sup> Likewise, our measured fusion and sublimation enthalpies at 298 K ( $5.468 \pm 0.047$  and  $25.41 \pm 0.67$  kcal mol<sup>-1</sup>, respectively) also are in good accord with earlier measurements of 5.423 and 23.5 kcal mol<sup>-1</sup> (no uncertainties given) at a mean temperature of 329 K.<sup>41,42</sup> Consequently, calorimetric experiments were carried out on **5** since *o*-benzoquinone is too reactive and unstable to carry out a direct determination of its enthalpy of formation via combustion calorimetry.

We obtained  $\Delta_f H^\circ(\text{cr}) = -98.45 \pm 0.81$  kcal mol<sup>-1</sup> and  $\Delta_{\text{cr}} H^\circ = 25.36 \pm 0.31$  kcal mol<sup>-1</sup> from our calorimetric experiments, and thus the gaseous standard molar enthalpy of formation of **5** is  $-73.09 \pm 0.87$  kcal mol<sup>-1</sup>. The enthalpy of sublimation is virtually identical to that for benzil (Table 2), which is not surprising since both species are 14-carbon  $\alpha$ -diketones.<sup>43</sup> As for the heat of formation, it needs to be transformed to make a meaningful comparison with the value for the parent species determined by ion energetic measurements. This was accomplished by computationally exploring the effect of *tert*-butyl groups in a series of isodesmic reactions (eqs 7–10). Removing one *tert*-butyl from **5** leads to 3-*tert*-butyl-*o*-benzoquinone (**6**) or 4-*tert*-butyl-*o*-benzoquinone (**7**, eq 7), and these two products are predicted to be equally stable (within 0.4 kcal mol<sup>-1</sup>) by B3LYP calculations.



1.7 B3LYP/6-31G(d), 2.1 B3LYP/6-311G(d,p); R = H, R' = *t*-Bu (**6**)  
 1.4 B3LYP/6-31G(d), 1.7 B3LYP/6-311G(d,p); R = *t*-Bu, R' = H (**7**)

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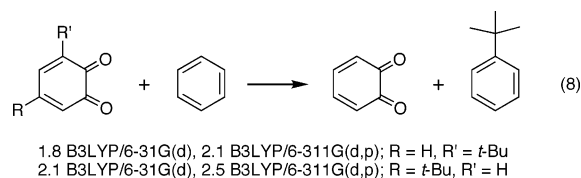
- (37) The computed heats of hydrogenation were obtained from the calculated heats of formation via atomization reactions.  
 (38) (a) Ribeiro Da Silva, M. D. M. C.; Ribeiro Da Silva, M. A. V. *J. Chem. Thermodyn.* **1984**, *16*, 1149–1155. Alternative sets of values for the ortho and meta compounds are  $-64.8 \pm 1.0$  and  $-66.9 \pm 1.1$ , respectively. See: (b) Slayden, S. W.; Liebman, J. F. In *The Chemistry of Phenols*; Rappaport, Z., Ed.; Wiley: New York, 2003; pp 223–257.  
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**Table 5.** Summary of Thermochemical Data Used for Ion Energetics<sup>a</sup>

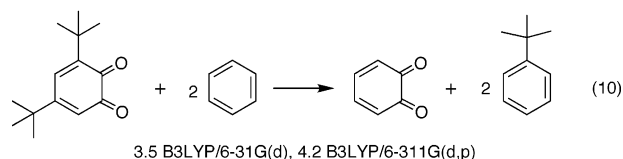
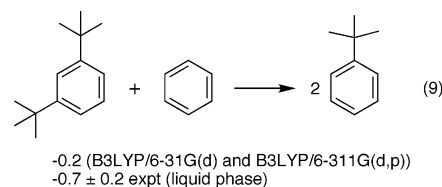
compd	$\Delta_{\text{acid}}H^\circ$		EA		BDE		$\Delta_fH^\circ$	
	expt	calcd	expt	calcd	expt	calcd	expt	calcd
<i>o</i> -benzoquinone			43.8 ± 3.0	46.2 (45.2)			-23.1 ± 4.1 -18.9 ± 2.2 <sup>g</sup> -21.0 ± 3.1 <sup>h</sup>	-19.7 (-17.4)
<i>m</i> -benzoquinone			65.0 ± 2.3	67.2 (66.4)			6.8 ± 4.1	8.4 (10.5)
<i>p</i> -benzoquinone			42.9 ± 0.1 <sup>c</sup>	44.2 (43.8)			-27.7 ± 3.0 -29.3 ± 0.9 <sup>b</sup>	-27.6 (-25.5)
<i>o</i> -benzoquinone* <sup>-</sup>							-66.9 ± 5.1 -64.8 ± 4.3 <sup>d</sup>	-65.9 (-67.1)
<i>m</i> -benzoquinone* <sup>-</sup>							-58.2 ± 4.7	-58.8 (-60.0)
<i>p</i> -benzoquinone* <sup>-</sup>							-70.6 ± 3.0 -72.2 ± 0.9 <sup>e</sup>	-71.8 (-73.5)
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (OH)O*	335.2 ± 2.0	336.9 (335.5)	55.6 ± 2.9	54.6 (56.6)	65.4 ± 3.6 67.5 ± 3.7 <sup>d</sup>	69.5 (67.1)	-36.4 ± 2.0	-36.3 (-39.5)
<i>m</i> -C <sub>6</sub> H <sub>4</sub> (OH)O*	338.6 ± 2.8	335.6 (337.4)	55.9 ± 2.9	55.0 (56.6)	90.0 ± 3.6	89.2 (90.2)	-31.1 ± 2.0	-27.9 (-31.2)
<i>p</i> -C <sub>6</sub> H <sub>4</sub> (OH)O*	331.1 ± 1.7	325.0 (326.5)	45.5 ± 3.3	46.5 (48.3)	60.4 ± 1.7 58.8 ± 2.7 <sup>e</sup>	55.6 (56.7)	-36.0 ± 2.5	-30.4 (-33.5)
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (OH)O <sup>-</sup>					77.2 ± 3.5 79.3 ± 4.8 <sup>d</sup>	77.9 (78.5)	-92.0 ± 2.1	-90.3 (-92.6)
<i>m</i> -C <sub>6</sub> H <sub>4</sub> (OH)O <sup>-</sup>					80.9 ± 4.0	77.0 (80.4)	-87.0 ± 2.1	-82.4 (-86.0)
<i>p</i> -C <sub>6</sub> H <sub>4</sub> (OH)O <sup>-</sup>					63.0 ± 3.7 61.4 ± 2.3 <sup>e</sup>	57.9 (61.2)	-81.5 ± 2.1	-77.0 (-80.1)
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub>	339.6 ± 2.1 <sup>b</sup>	339.7 (340.7)			81.6 ± 2.0 <sup>f</sup>	80.8 (81.4)	-65.9 ± 0.3 <sup>j</sup>	-64.3 (-61.0)
<i>m</i> -C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub>	346.7 ± 2.1 <sup>b</sup>	347.1 (346.7)			89.0 ± 2.0 <sup>f</sup>	88.6 (89.5)	-68.0 ± 0.3 <sup>j</sup>	-63.8 (-60.5)
<i>p</i> -C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub>	350.4 ± 2.1 <sup>b</sup>	350.3 (350.5)			82.3 ± 2.5 <sup>f</sup>	84.0 (84.8)	-66.2 ± 0.3 <sup>j</sup>	-61.6 (-58.5)

<sup>a</sup> All values are in kcal mol<sup>-1</sup> and come from our ion energetic determinations unless otherwise noted. Computed energies were obtained using G3 theory as described in the text. <sup>b</sup> Values taken from ref 7. <sup>c</sup> Reference 34. <sup>d</sup> Based upon our recommended value for the heat of formation of *o*-benzoquinone. <sup>e</sup> This value was obtained using the enthalpy of formation of *p*-benzoquinone given in ref 7. <sup>f</sup> Reference 36. <sup>g</sup> From combustion calorimetry and B3LYP computations; see text for additional details. <sup>h</sup> Our recommended value. <sup>i</sup> Reference 38.

This is not surprising since the *tert*-butyl group can stabilize the partial positive charge on the carbon to which it is attached (i.e., **7** can be viewed as a  $\beta$ -substituted  $\alpha,\beta$ -unsaturated ketone and **6** is its vinylogous derivative). De-*tert*-butylation of **6** and **7** leads to the parent benzoquinone (eq 8).



Interestingly, these processes are predicted to have the same reaction energies to within 0.4 kcal mol<sup>-1</sup> as those in eq 7, indicating that the effect of the two *tert*-butyl groups is additive. To test this result, the de-*tert*-butylation of 1,3-di-*tert*-butylbenzene was considered and found to be nearly thermoneutral (eq 9), in accord with the observed equilibration of these hydrocarbons in condensed media under acidic conditions.<sup>44</sup> Consequently, we use the average of the 6-31G(d) and 6-311G(d,p) B3LYP energies for eq 10 ( $\Delta_{\text{rxn}}H^\circ = 3.8$  kcal mol<sup>-1</sup>) along with our determination of the heat of formation of 3,5-di-*tert*-butyl-*o*-benzoquinone and the literature value ( $-5.4 \pm 0.3$  kcal mol<sup>-1</sup>)<sup>7</sup> for *tert*-butylbenzene to give  $\Delta_fH^\circ(\mathbf{1o}) = -18.9$  kcal mol<sup>-1</sup> with a plausible uncertainty of  $\pm 2.2$  kcal mol<sup>-1</sup>.<sup>45</sup>



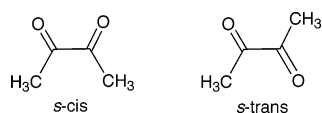
This result is in good accord with our determination via ion-energetic measurements ( $-23.1 \pm 4.1$  kcal mol<sup>-1</sup>), and our recommended value for the heat of formation of *o*-benzoquinone is the average of these two determinations or  $-21.0 \pm 3.1$  kcal mol<sup>-1</sup>. The computed G3 heat of formation using the atomization energy of *o*-benzoquinone is  $-19.7$  ( $-17.4$ ) kcal mol<sup>-1</sup>, which is in excellent agreement with our result. We also obtain an experimental difference of  $8.3 \pm 3.2$  kcal mol<sup>-1</sup> between **1o** and **1p**, which is well-reproduced by theory (7.9 (8.1) G3, 6.9 B3LYP/6-31G(d), and 7.1 B3LYP/6-311G(d,p) kcal mol<sup>-1</sup>) and can be accounted for by the repulsion of the electrons on the adjacent oxygen atoms in the ortho derivative. In this regard, it is worth noting that, according to G3 theory, biacetyl is less stable in its *s*-cis configuration than the *s*-trans form (Chart 2) by 6.6 kcal mol<sup>-1</sup> at 0 K.

**Auxiliary Data.** The O–H bond dissociation energies of all three dihydroxybenzenes are known (Table 5), and if these results are combined with our energetic determinations for *o*- and *m*-benzoquinone and the literature value for the heat of formation of *p*-benzoquinone, second O–H bond energies of  $67.5 \pm 3.7$  (**o**),  $90.0 \pm 3.6$  (**m**), and  $58.8 \pm 2.7$  (**p**) are obtained.

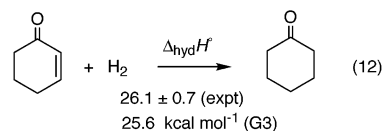
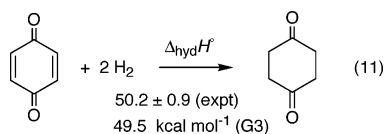
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Chart 2



These results are in excellent accord with the G3 predictions of 69.5 (67.1) (**o**), 89.2 (90.2) (**m**), and 55.6 (56.7) kcal mol<sup>-1</sup> (**p**). As expected, additivity applies for triplet biradical **1m**, and the first and second O–H bond energies of 1,3-dihydroxybenzene are the same within the experimental uncertainty.<sup>46</sup> In contrast, **1o** and **1p** are singlets, and greatly reduced BDE2s are expected for such species because a  $\pi$  bond results. For example, the differences in the first and second bond energies for ethane and methanol are 65.5  $\pm$  0.6 and 69.9  $\pm$  0.3 kcal mol<sup>-1</sup>, respectively.<sup>7c,47</sup> However, for **1o** and **1p**, BDE1 – BDE2 is only 14.1  $\pm$  4.2 and 23.5  $\pm$  3.7 kcal mol<sup>-1</sup>, respectively. These unusually small values indicate that both quinones are excellent radical traps from a thermodynamic perspective<sup>48</sup> and largely arise because of the  $\sim$ 40 kcal mol<sup>-1</sup> loss in aromaticity upon removing the second hydrogen from the dihydroxybenzene; the resonance energy of phenol is 39.9  $\pm$  1.2 kcal mol<sup>-1</sup> if one compares its heat of hydrogenation (45.34  $\pm$  0.47 kcal mol<sup>-1</sup>) to 3 times that for cyclohexene (3  $\times$  28.41  $\pm$  0.37 = 85.23  $\pm$  1.17 kcal mol<sup>-1</sup>).<sup>7</sup> Aromaticity or antiaromaticity of the quinones, both of which have been suggested,<sup>4</sup> also would have an effect. If one compares the experimental heat of hydrogenation for the carbon–carbon double bonds in *p*-benzoquinone (eq 11)<sup>7,49</sup> to twice that for 2-cyclohexen-1-one (eq 12),<sup>50</sup> then the 2.0  $\pm$  1.1 kcal mol<sup>-1</sup> difference, which is well-reproduced by G3 theory (1.7 kcal mol<sup>-1</sup>), clearly indicates that **1p** (and thus **1o**) are nonaromatic.<sup>51</sup>



## Conclusions

*o*-, *m*-, and *p*-Benzoquinone radical anions were generated in a Fourier transform mass spectrometer, and their proton affinities and electron binding energies were measured. These data in conjunction with thermodynamic cycles enable the heats of formation of the corresponding neutral quinones to be deter-

mined. Our result for *p*-benzoquinone ( $\Delta_f H^\circ = -27.7 \pm 3.0$  kcal mol<sup>-1</sup>) is in excellent accord with the well-established literature value of  $-29.3 \pm 0.9$  kcal mol<sup>-1</sup> and a G3 theory prediction of  $-27.6$  ( $-25.5$ ) kcal mol<sup>-1</sup>. Calorimetric measurements of the heats of combustion and sublimation for 3,5-di-*tert*-butyl-*o*-benzoquinone provided its heat of formation in the gas phase, and in conjunction with the B3LYP/6-31G(d) and B3LYP/6-311G(d,p) energies for an isodesmic de-*tert*-butylation reaction (eq 10),  $\Delta_f H^\circ(\mathbf{1o}) = -18.9 \pm 2.2$  kcal mol<sup>-1</sup> was obtained. This independent determination is in good accord with the directly determined value of  $-23.1 \pm 4.1$  kcal mol<sup>-1</sup> via ion-energetic measurements and leads to an averaged and recommended value of  $-21.0 \pm 3.1$  kcal mol<sup>-1</sup>, which also is well-reproduced by G3 theory ( $-19.7$  ( $-17.4$ ) kcal mol<sup>-1</sup>). Finally, *m*-benzoquinone has a heat of formation of  $6.8 \pm 4.1$  kcal mol<sup>-1</sup>, which is essentially the same as that predicted by additivity ( $5.8 \pm 2.8$  kcal mol<sup>-1</sup>) (i.e., assuming that the first and second O–H bond energies for 1,3-dihydroxybenzene are equal) as might be expected for a ground-state triplet molecule. This result also is well-reproduced by G3 theory ( $\Delta_f H^\circ = 8.4$  (10.5) kcal mol<sup>-1</sup>).

From the data in this work, one can also derive the second O–H bond energies for 1,2- and 1,4-dihydroxybenzene and compare the results to first bond strengths. Both the individual values and the differences ( $81.6 \pm 2.0 - 67.5 \pm 3.7 = 14.1 \pm 4.2$  kcal mol<sup>-1</sup> (*o*) and  $82.3 \pm 2.5 - 58.8 \pm 2.7 = 23.5 \pm 3.7$  kcal mol<sup>-1</sup> (*p*)) are in good accord with G3 predictions (BDE1 = 80.8 (81.4) (*o*), 84.0 (84.8) (*p*) kcal mol<sup>-1</sup> and BDE2 = 69.5 (67.1) (*o*), 55.6 (56.7) (*p*) kcal mol<sup>-1</sup>), but the latter results are seemingly small given that a new  $\pi$  bond is being formed. This “discrepancy” can largely be accounted for by the loss of aromaticity upon removal of the second hydrogen atom, which amounts to  $\sim$ 40 kcal mol<sup>-1</sup>. It is not a result of forming an aromatic compound as *o*- and *p*-benzoquinone are nonaromatic. The unusually large second BDE makes both quinones excellent radical traps from a thermodynamic perspective and undoubtedly is important in regulating quinone–hydroquinone concentrations in biological systems.

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