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# $\alpha,2-$ , $\alpha,3-$ , and $\alpha,4$ -Dehydrophenol Radical Anions: Formation, Reactivity, and Energetics Leading to the Heats of Formation of $\alpha,2-$ , $\alpha,3-$ , and $\alpha,4$ -Oxocyclohexadienylidene

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# $\alpha,2-$ , $\alpha,3-$ , and $\alpha,4-$ Dehydrophenol Radical Anions: Formation, Reactivity, and Energetics Leading to the Heats of Formation of $\alpha,2-$ , $\alpha,3-$ , and $\alpha,4-$ Oxocyclohexadienyldiene

## Abstract

We have regiospecifically generated the  $\alpha,2-$ ,  $\alpha,3-$ , and  $\alpha,4-$ dehydrophenoxide anions by collisional activation of *o*-, *m*-, and *p*-nitrobenzoate. The  $\alpha,2$  and  $\alpha,4$  isomers also were synthesized by reacting *o*-benzyne radical anion with carbon dioxide and electron ionization of *o*-diazophenol. All three dehydrophenol radical anions were differentiated from each other and identified by probing their chemical reactivity with several reagents. Each isomer was converted to phenoxide and its corresponding quinone as well. Thermochemical measurements were carried out on all three radical anions and their hydrogen-atom affinities, proton affinities, and electron binding energies are reported. These measured quantities are combined in thermodynamic cycles to derive the heats of formation of each of the radical anions and their corresponding carbenes (i.e.,  $\alpha,2-$ ,  $\alpha,3-$ , and  $\alpha,4-$ dehydrophenol). These results are compared to MCQDPT2, G3, G2+(MP2), and B3LYP calculations and experimental data for appropriate reference compounds.

## Disciplines

Chemistry

## Comments

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## $\alpha,2$ -, $\alpha,3$ -, and $\alpha,4$ -Dehydrophenol Radical Anions: Formation, Reactivity, and Energetics Leading to the Heats of Formation of $\alpha,2$ -, $\alpha,3$ -, and $\alpha,4$ -Oxocyclohexadienylidene

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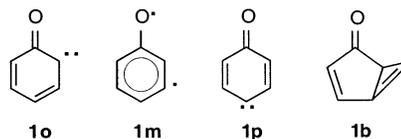
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**Abstract:** We have regiospecifically generated the  $\alpha,2$ -,  $\alpha,3$ -, and  $\alpha,4$ -dehydrophenoxide anions by collisional activation of *o*-, *m*-, and *p*-nitrobenzoate. The  $\alpha,2$  and  $\alpha,4$  isomers also were synthesized by reacting *o*-benzyne radical anion with carbon dioxide and electron ionization of *p*-diazophenol. All three dehydrophenol radical anions were differentiated from each other and identified by probing their chemical reactivity with several reagents. Each isomer was converted to phenoxide and its corresponding quinone as well. Thermochemical measurements were carried out on all three radical anions and their hydrogen-atom affinities, proton affinities, and electron binding energies are reported. These measured quantities are combined in thermodynamic cycles to derive the heats of formation of each of the radical anions and their corresponding carbenes (i.e.,  $\alpha,2$ -,  $\alpha,3$ -, and  $\alpha,4$ -dehydrophenol). These results are compared to MCQDPT2, G3, G2+(MP2), and B3LYP calculations and experimental data for appropriate reference compounds.

### Introduction

Carbenes are formed in many useful chemical transformations and have been the subject of extensive experimental investigations.<sup>1</sup> They also provide a demanding testing ground for computational methods and, consequently, have been the focus of a large number of theoretical studies. Diazo precursors of *p*-oxocyclohexadienylidene (**1p**) and its derivatives (i.e., quinonediazides) are particularly important compounds as they are used in technological processes such as photolithography, the stabilization of rubbers, polyolefins, diesel fuels, and lubricating oils, and the preservation of foods and fats.<sup>2</sup> The parent carbene,  $\alpha,4$ -dehydrophenol (**1p**), has been generated in solution both

thermally and photochemically from 4-diazo-2,5-cyclohexadienone.<sup>3</sup> It was found to be a ground-state triplet on the basis of the observed low-temperature ESR signal.<sup>3b</sup> From an analysis of the spectrum at 4 K the spin density at the para carbon (C4) was found to be 0.42–0.45, which is similar to the value for phenoxyl radical (0.4) at the same site. This led to the suggestion that **1p** is a  $\sigma^1\pi^1$  diradical, which has the  $\pi$ -system of a phenoxyl radical and the  $\sigma$ -system of phenyl radical. In accord with this view, Sander and co-workers found that the carbon–oxygen bond stretch in the matrix-isolated IR spectrum of **1p** is at 1496  $\text{cm}^{-1}$ .<sup>3d</sup> This frequency is about halfway between the C–O single and double bond stretches of phenol (1250  $\text{cm}^{-1}$ ) and *p*-quinone (1682  $\text{cm}^{-1}$ ) and leads to a bond order of  $\sim 1.5$ .



Recently, multiconfiguration self-consistent field (MCSCF) calculations have been carried out on  $\alpha,2$ -,  $\alpha,3$ -, and  $\alpha,4$ -

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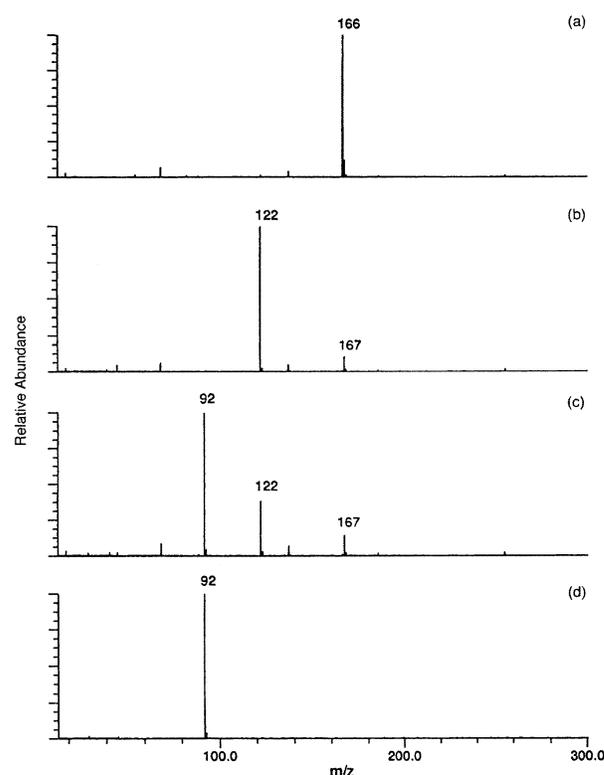
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oxocyclohexadienylidene (**1o**, **1m**, and **1p**).<sup>4</sup> The ground electronic states of the  $\alpha,2$  and  $\alpha,4$  isomers were found to be open-shell triplets with singlet–triplet (S–T) gaps of 8.7 and 10.6 kcal mol<sup>-1</sup>, respectively, using multiconfiguration quasi-degenerate second-order perturbation theory (MQDPT2/6-311+G(d)//MCSCF(8,8)/6-31+G(d)). In contrast, the  $\alpha,3$  or meta isomer **1m** is predicted to be a ground-state singlet with a small S–T gap of 0.6 kcal mol<sup>-1</sup>. All three isomers are structurally similar and have short carbon–oxygen bonds (1.216–1.230 Å) and distinct carbon–carbon bond lengths spanning a range of 0.089–0.137 Å. These geometries suggest that **1o**, **1m**, and **1p** are best described as quinoid-type biradicals. From an energetic point of view, the relative ground-state energies of these carbenes are predicted to be nearly the same (1.1 (**1p**), 0.0 (**1m**), and 2.9 (**1o**) kcal mol<sup>-1</sup>).<sup>5</sup> Based upon an estimate for the heat of formation of 1*H*-bicyclo[3.1.0]hexa-3,5-dien-2-one (**1b**) by Sander et al. (57 kcal mol<sup>-1</sup>),<sup>3e</sup> the computed energy difference between this compound and **1p** reported by Sole et al. (19 kcal mol<sup>-1</sup>),<sup>4a</sup> and the relative energies of **1o**, **1m**, and **1p**, one can obtain 40, 37, and 38 kcal mol<sup>-1</sup> for the respective heats of formation of these carbenes. These estimates are markedly different from the value obtained by assuming bond additivity (75 ± 1 kcal mol<sup>-1</sup>) and indicate that something is amiss. No experimental data, however, are available to determine where the error(s) lies.

An electron can serve as a protecting group, and as such, gas-phase negative ion chemistry can provide thermodynamic information on neutral, uncharged, species.<sup>6</sup> This approach is particularly valuable for obtaining the energetics of transient molecules because it is difficult to do this by other methods. Radical anions are needed to obtain information on carbenes and biradicals, and we recently described a general method for their preparation.<sup>6a</sup> In the process of developing this methodology, we rediscovered that the collision-induced fragmentation of *o*-, *m*-, and *p*-nitrobenzoate (**2**) leads to the sequential loss of carbon dioxide and nitric oxide.<sup>7</sup> This sequence violates the “even-electron rule” and affords radical anions with mass-to-charge ratios of 92. We now report on the formation and structural authentication of  $\alpha,2$ -,  $\alpha,3$ -, and  $\alpha,4$ -dehydrophenol radical anions (**3o**, **3m**, and **3p**) along with energetic measurements that lead to a determination of the heats of formation of the corresponding biradicals. G3, G2+(MP2), B3LYP, and MCQDPT2 calculations also were carried out to compare with the experimental results.

## Experimental Section

Gas-phase experiments were carried out with a Finnigan model 2001 Fourier transform mass spectrometer (FTMS), which previously has



**Figure 1.** (a) Deprotonation of *p*-nitrobenzoic acid with F<sup>-</sup>; *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub><sup>-</sup> (**2p**, *m/z* 166). (b) Formation of *p*-nitrophenide (*m/z* 122) via 5–6 eV sustained off-resonance irradiation of **2p**; the ion at *m/z* 167 is the residual <sup>13</sup>C isotopomer of *p*-nitrobenzoate. (c) Immediate application of a second 2–3 eV SORI excitation causing the loss of nitric oxide and the formation of *p*-dehydrophenoxide radical anion (**3p**, *m/z* 92). (d) Isolation of **3p** for further study via ion–molecule reactions.

been described.<sup>6a</sup> Briefly, our instrument is equipped with a dual cell inside the bore of a 3-T superconducting magnet and is outfitted with an Ultrasource electrostatic ion guide interfaced to an Analytica electrospray ionization (ESI) source. Ions were initially generated by electron ionization or ESI and the desired species were isolated by using stored-waveform inverse Fourier transform (SWIFT) and/or chirp excitations.<sup>8,9</sup> Translational and vibrational cooling of the ions was carried out by collisions with argon, which was pulsed into the appropriate cell up to pressures of ~1 × 10<sup>-4</sup> Torr. Neutral reagents were added via pulsed or slow leak valves, and all reactions were monitored as a function of time.

**Generation of  $\alpha,2$ -,  $\alpha,3$ -, and  $\alpha,4$ -Dehydrophenoxide Radical Anions by Collision-Induced Dissociation of *o*-, *m*-, and *p*-Nitrobenzoate.** *o*-, *m*-, and *p*-Nitrobenzoic acid were purchased from Aldrich Chemical Co. and used without further purification. In separate experiments each of these acids was admitted into the source cell of the FTMS via the solids inlet probe. Upon heating to 100–120 °C each acid had sufficient vapor pressure to react with fluoride ion to afford an abundant signal of its conjugate base (Figure 1). The resulting carboxylate anions were transferred to the analyzer cell and fragmented in the presence of argon (~10<sup>-5</sup> Torr) by sustained off-resonance irradiation (SORI)<sup>10</sup> at excitation energies between 5 and 6 eV. Each newly produced nitrophenide ion was subjected to a second SORI pulse at 2–3 eV to bring about the loss of nitric oxide. The energy for the latter fragmentation was carefully optimized in each experiment because insufficient fragmentation takes place if the energy is too low and nitrite

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anion ( $\text{NO}_2^-$ ) is formed at higher energies. Isolation of the resulting  $\text{C}_6\text{H}_4\text{O}^-$  ( $m/z$  92) ions were carried out by a combination of SWIFT and chirp excitation pulses,<sup>8,9</sup> and these ions were subsequently cooled with argon pulsed to a pressure of  $\sim 10^{-4}$  Torr. In some experiments, the carboxylate anions were prepared by ESI of the conjugate acid from a 1:1 methanol–water solution (v/v) containing 0.1% ammonia.

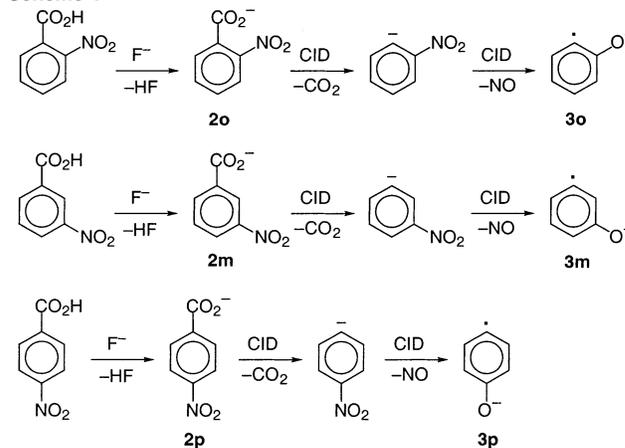
**Generation of  $\alpha,4$ -Dehydrophenoxide Radical Anion by Dissociative Electron Capture of 4-Diazo-2,5-cyclohexadienone.** 4-Diazo-2,5-cyclohexadienone was prepared by literature methods and stored at  $-40$  °C in the dark.<sup>11</sup> The wet diazide was dried in the sample lock of the solids probe at  $\sim 10^{-2}$  Torr and then was introduced into the high vacuum system. After briefly heating the sample to  $40$  °C to drive off residual water, it was ionized with  $6$  eV electrons to afford a  $\text{C}_6\text{H}_4\text{O}^-$  anion at  $m/z$  92. This ion was subsequently transferred to the analyzer cell where it was cooled with a pulse of argon ( $\sim 10^{-4}$  Torr) and isolated for further investigation.

**Generation of  $\alpha,2$ -Dehydrophenoxide Radical Anion by Oxygen Atom Transfer to *o*-Benzyne Radical Anion.** Atomic oxygen radical anion was generated by dissociative electron impact on nitrous oxide and then was reacted with benzene to afford *o*-benzyne radical anion.<sup>12</sup> This ion was allowed to react with a static pressure of carbon dioxide ( $\sim 10^{-7}$  Torr) in the source cell and at these low pressures oxygen atom transfer takes place in preference to adduct formation. The resulting  $\alpha,2$ -dehydrophenoxide radical anion was transferred to the analyzer cell where it was cooled with argon ( $\sim 10^{-4}$  Torr) and isolated for further investigation.

**Structure Authentication.** Each of the  $\text{C}_6\text{H}_4\text{O}^-$  isomers was converted into phenoxide ion by reaction with *tert*-butyl mercaptan or diethylhydroxylamine. The resulting hydrogen atom transfer product was bracketed with standard reference acids and further characterized by collision-induced dissociation (CID). These results were compared to control experiments performed on authentic phenoxide ion generated by fluoride anion deprotonation of phenol. The  $\alpha,2$ - and  $\alpha,4$ -isomers also were derivatized to the corresponding quinone radical anions by reaction with sulfur dioxide. These latter species were characterized by bracketing their electron binding energies and comparing the results to the known electron affinities of *o*- and *p*-quinone.

**Computations.** All calculations were carried out using GAMESS<sup>13</sup> and Gaussian 98<sup>14</sup> or earlier versions of the program on SGI and IBM workstations. Geometries were optimized at the HF and MP2 levels with the 6-31G(d) and 6-31+G(d) basis sets. Closed-shell systems were treated by using restricted wave functions and open-shell species were handled by using the unrestricted formalism. In both cases, analytical vibrational frequencies were computed at both theoretical levels for each stationary point. Zero-point energies and temperature corrections to 298 K were computed by scaling the vibrational frequencies using the following factors: 0.9135 (HF, ZPE), 0.8929 (HF,  $\nu$ 's), 0.9646 (MP2, ZPE), and 0.9427 (MP2,  $\nu$ 's), where ZPE refers to the vibrational zero-point energy correction.<sup>15</sup> All of the cited energies in this work

Scheme 1



include ZPE corrections and are at 0 K (electron affinities) or 298 K (proton affinities and bond dissociation energies).

In an attempt to obtain reliable energetic data and to assess several popular computational approaches, B3LYP/6-311+G(3df,2p)/MP2/6-31+G(d), G2+(MP2),<sup>16</sup> and G3<sup>17</sup> calculations were carried out. The second of these methods effectively corresponds to a QCISD(T)/6-311+G(3df,2p) energy but was obtained on a MP2(FC)/6-31+G(d) geometry as follows:

$$E[\text{G2}+(\text{MP2})] = E[\text{QCISD}(\text{T})/6-311+\text{G}(\text{d,p})] + E[\text{MP2}/6-311+\text{G}(3\text{df},2\text{p})] - E[\text{MP2}/6-311+\text{G}(\text{d,p})] + \text{hlc} + \text{ZPE} + \text{TC} \quad (1)$$

where hlc is the high level correction term for G2 theory and TC is a temperature correction to 298 K. Hartree–Fock ZPEs and vibrational frequencies for the temperature corrections were used in each case, but in some instances there are significant differences ( $\geq 1.0$  kcal mol<sup>-1</sup>) with the MP2 corrections. In these situations both sets of results are given.

As the species of interest in this work are inherently multiconfigurational, MCSCF geometries and Hessians also were computed with the 6-31G(d) and 6-31+G(d) basis sets.<sup>18</sup> To account for some of the dynamic correlation in these species, single-point calculations were carried out at the MCQDPT2 level with the 6-311+G(d) basis set. All of the resulting energies were ZPE corrected and adjusted to 298 K, except for the electron affinities which are at 0 K, by using unscaled MCSCF vibrational frequencies.

## Results and Discussion

Deprotonation of *o*-, *m*-, and *p*-nitrobenzoic acid by fluoride ion in the gas phase affords the corresponding carboxylate anions (**2**), which lose carbon dioxide upon 5–6 eV SORI–CID. Further fragmentation of the phenide isomers at 2–3 eV yields the desired  $\alpha,2$ -,  $\alpha,3$ -, and  $\alpha,4$ -dehydrophenoxide radical anions (Scheme 1 and Figure 1). These cleavages previously have been reported in the analytical chemistry literature,<sup>7</sup> but the structures and reactivities of the resulting  $\text{C}_6\text{H}_4\text{O}^-$  ions were not explored. To establish the structures of **3o**, **3m**, and **3p**, their reactivities were examined. It was anticipated that these radical anions should have the  $\sigma$ -system of a phenyl radical and the  $\pi$ -system of a phenoxide ion and would display radical reactivity similar to related distonic radical cations containing an aryl radical moiety. In accord with these expectations, all three isomers

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**Table 1.** Reaction Products of **3o**, **3m**, and **3p** with Probe Reagents<sup>a</sup>

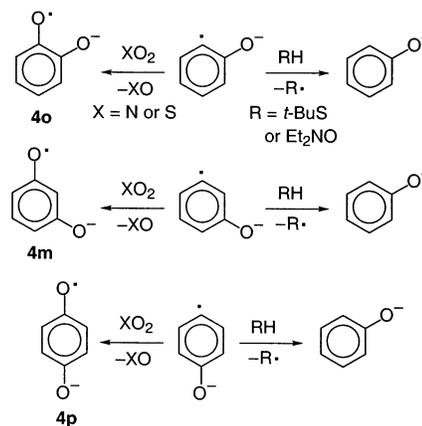
reagent	observed products		
	3o	3m	3p
MeSSMe	<i>o</i> -MeSC <sub>6</sub> H <sub>4</sub> O <sup>-</sup> (139)	<i>m</i> -MeSC <sub>6</sub> H <sub>4</sub> O <sup>-</sup> (139)	<i>p</i> -MeSC <sub>6</sub> H <sub>4</sub> O <sup>-</sup> (139)
CCl <sub>4</sub>	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> O <sup>-</sup> (127, 66%), CCl <sub>3</sub> <sup>-</sup> (117, 33%)	<i>m</i> -ClC <sub>6</sub> H <sub>4</sub> O <sup>-</sup> (127, 60%), CCl <sub>3</sub> <sup>-</sup> (117, 40%)	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> O <sup>-</sup> (127, 66%), CCl <sub>3</sub> <sup>-</sup> (117, 33%)
NO	<i>o</i> -ONC <sub>6</sub> H <sub>4</sub> O <sup>-</sup> (122)	<i>m</i> -ONC <sub>6</sub> H <sub>4</sub> O <sup>-</sup> (122, 70%), <i>m</i> -OC <sub>6</sub> H <sub>4</sub> O <sup>-</sup> (108, 3%), CN <sup>-</sup> (26, 6%), NO <sub>2</sub> <sup>-</sup> (46, 15%), C <sub>4</sub> H <sub>4</sub> N <sup>-</sup> (66, 7%)	<i>p</i> -ONC <sub>6</sub> H <sub>4</sub> O <sup>-</sup> (122)
SO <sub>2</sub>	<i>o</i> -OC <sub>6</sub> H <sub>4</sub> O <sup>-</sup> (108)	<i>m</i> -OC <sub>6</sub> H <sub>4</sub> O <sup>-</sup> (108, ~33%), <i>m</i> -OC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> <sup>-</sup> (156, ~66%) <sup>b</sup>	<i>p</i> -OC <sub>6</sub> H <sub>4</sub> O <sup>-</sup> (108)
NO <sub>2</sub>	NO <sub>2</sub> <sup>-</sup> (46, 58%), <i>o</i> -OC <sub>6</sub> H <sub>4</sub> O <sup>-</sup> (108, 38%), C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> <sup>-</sup> (122, 4%)	NO <sub>2</sub> <sup>-</sup> (46, 40%), <i>m</i> -OC <sub>6</sub> H <sub>4</sub> O <sup>-</sup> (108, 50%), C <sub>5</sub> H <sub>4</sub> O <sup>-</sup> (80, 10%)	NO <sub>2</sub> <sup>-</sup> (46, 48%), <i>p</i> -OC <sub>6</sub> H <sub>4</sub> O <sup>-</sup> (108, 48%), C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> <sup>-</sup> (122, 4%)
COS	<i>o</i> -SC <sub>6</sub> H <sub>4</sub> O <sup>-</sup> (124)	<i>m</i> -SC <sub>6</sub> H <sub>4</sub> O <sup>-</sup> (124, ~66%), <i>m</i> -OC <sub>6</sub> H <sub>4</sub> COS <sup>-</sup> (152, ~33%)	<i>p</i> -SC <sub>6</sub> H <sub>4</sub> O <sup>-</sup> (124, ~66%), <i>p</i> -OC <sub>6</sub> H <sub>4</sub> COS <sup>-</sup> (152, ~33%)
<i>t</i> -BuSH	<i>t</i> -BuS <sup>-</sup> (89, 20%), C <sub>6</sub> H <sub>5</sub> O <sup>-</sup> (93, 70%), <i>o</i> -SC <sub>6</sub> H <sub>4</sub> OH <sup>-</sup> (125, 10%)	<i>t</i> -BuS <sup>-</sup> (89, 35%), C <sub>6</sub> H <sub>5</sub> O <sup>-</sup> (93, 60%), <i>m</i> -HSC <sub>6</sub> H <sub>4</sub> O <sup>-</sup> (125, 5%)	<i>t</i> -BuS <sup>-</sup> (89, 20%), C <sub>6</sub> H <sub>5</sub> O <sup>-</sup> (93, 75%), <i>p</i> -HSC <sub>6</sub> H <sub>4</sub> O <sup>-</sup> (125, 5%)
maleic anhydride	C <sub>8</sub> H <sub>6</sub> O <sup>-</sup> (118, 50%), C <sub>4</sub> HO <sub>3</sub> <sup>-</sup> (97, 20%), C <sub>9</sub> H <sub>5</sub> O <sub>2</sub> <sup>-</sup> (145, 20%), C <sub>9</sub> H <sub>4</sub> O <sub>2</sub> <sup>-</sup> (146, 10%)	C <sub>9</sub> H <sub>5</sub> O <sub>2</sub> <sup>-</sup> (145, 80%), C <sub>9</sub> H <sub>4</sub> O <sub>2</sub> <sup>-</sup> (146, 20%)	C <sub>8</sub> H <sub>6</sub> O <sup>-</sup> (118, 45%), C <sub>4</sub> HO <sub>3</sub> <sup>-</sup> (97, 25%), C <sub>9</sub> H <sub>5</sub> O <sub>2</sub> <sup>-</sup> (145, 20%), C <sub>9</sub> H <sub>4</sub> O <sub>2</sub> <sup>-</sup> (146, 10%)
Me <sub>3</sub> SiSiMe <sub>3</sub> <i>p</i> -benzoquinone	C <sub>12</sub> H <sub>6</sub> O <sub>2</sub> <sup>-</sup> (182, 33%), C <sub>12</sub> H <sub>7</sub> O <sub>2</sub> <sup>-</sup> (183, 66%)	C <sub>12</sub> H <sub>8</sub> O <sub>3</sub> <sup>-</sup> (200, 50%), C <sub>11</sub> H <sub>8</sub> O <sub>2</sub> <sup>-</sup> (172, 50%)	<i>p</i> -Me <sub>3</sub> SiC <sub>6</sub> H <sub>4</sub> O <sup>-</sup> (165) C <sub>12</sub> H <sub>8</sub> O <sub>3</sub> <sup>-</sup> (200, 50%), C <sub>11</sub> H <sub>8</sub> O <sub>2</sub> <sup>-</sup> (172, 50%)

<sup>a</sup> Values in parentheses correspond to the mass-to-charge ratio of the product ion followed by its percent abundance. <sup>b</sup> The product ratio was obtained at  $1.1 \times 10^{-7}$  Torr of SO<sub>2</sub> and is sensitive to this pressure.

undergo a number of atom and group transfers with a variety of reagents (Table 1). This type of behavior has been observed with radicals in condensed media and with other radical anions and cations in the gas phase.<sup>6a,6d,19</sup>

**Structural Verification.** All three dehydrophenol radical anions can be differentiated on the basis of their qualitative reactivity with the probe reagents listed in Table 1. The  $\alpha,3$  isomer is the easiest one to differentiate in the group. For example, it reacts ~50 times slower with sulfur dioxide than the  $\alpha,2$  and  $\alpha,4$  radical anions and gives two product ions as opposed to one (i.e., oxygen-atom transfer and an adduct vs only the former reaction channel). The reactivity of **3m** with maleic anhydride also is distinct in that no (adduct-CO-CO<sub>2</sub>)<sup>-</sup> ( $m/z$  118) is observed from the  $\alpha,3$  isomer, whereas this is the major product ion from **3o** and **3p**. Reaction of *p*-benzoquinone with the three dehydrophenol radical anions serves to differentiate **3o** from **3m** and **3p**. In particular, **3o** gives (adduct-HO)<sup>-</sup> and (adduct-H<sub>2</sub>O)<sup>-</sup> ions ( $m/z$  183 and 182, respectively) whereas the other two isomers do not.

To further characterize the structures of **3o**, **3m**, and **3p**, they were converted to phenoxide ion ( $m/z$  92) upon reaction with *tert*-butyl mercaptan or diethylhydroxylamine (Scheme 2). In each case the identity of the phenoxide ion was verified by bracketing its proton affinity and fragmenting it by CID. All of the derivatized dehydrophenoxide radical anions and independently prepared phenoxide, generated by deprotonating phenol with F<sup>-</sup>, displayed identical behavior. In particular, these ions deprotonate acetic acid ( $\Delta H^{\circ}_{\text{acid}} = 348.1 \pm 2.2$  kcal mol<sup>-1</sup>) but not 2-methyl-2-propanethiol ( $\Delta H^{\circ}_{\text{acid}} = 352.5 \pm 2.2$  kcal mol<sup>-1</sup>), which is in accord with the literature proton affinity of

**Scheme 2**

$350.4 \pm 0.6$  kcal mol<sup>-1</sup> for phenoxide anion.<sup>20</sup> Likewise, all of the CID spectra show that C<sub>5</sub>H<sub>5</sub><sup>-</sup> is the dominant fragment at low energies (~50%) and that smaller amounts of C<sub>3</sub>H<sub>3</sub><sup>-</sup> (~35%), HC≡CO<sup>-</sup> (<10%), and HC≡C<sup>-</sup> (<10%) are formed. At higher energies, the cyclopentadienide fragment decreases in intensity relative to ketene enolate. These results preclude ring-opened structures for **3o**, **3m**, and **3p** and, given their unique reactivity, the three isomers cannot be interconverting between each other.

As a final structural confirmation to prove the structures of **3o**, **3m**, and **3p** beyond a reasonable doubt, they were converted to their corresponding benzoquinones upon reaction with sulfur dioxide or nitrogen dioxide (Scheme 2). The resulting benzoquinone radical anions (**4o**, **4m**, and **4p**) were characterized by

(19) (a) Heidbrink, J. L.; Ramirez-Arizmendi, L.; Thoen, K. K.; Guler, L.; Kenttamaa, H. I. *J. Phys. Chem. A* **2001**, *105*, 7875–7884. (b) Kochi, J. In *Free Radicals*; Wiley: New York, 1973.

(20) All thermodynamic data unless otherwise noted comes from: Bartmess, J. E. NIST Chemistry WebBook, NIST Standard Reference Database Number 69, W. G. Mallard and P. J. Linstrom (Eds.). In *Secondary NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, W. G. Mallard and P. J. Linstrom (Eds.), National Institute of Standards and Technology, Gaithersburg, MD 20899 (<http://webbook.nist.gov>).

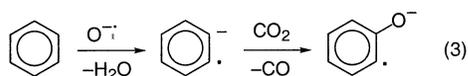
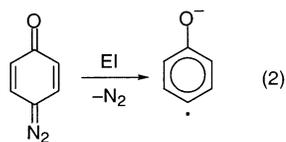
**Table 2.** Electron Affinity Bracketing Results for **1o**, **1m**, and **1p**

reagent	EA, eV	electron transfer		
		<b>3o</b>	<b>3m</b>	<b>3p</b>
SO <sub>2</sub>	1.107 ± 0.008	no	no	no
3-trifluoromethylnitrobenzene	1.41 ± 0.10	no	no	no
maleic anhydride	1.44 ± 0.09	no	no	no
3,5-bis(trifluoromethyl)-nitrobenzene	1.79 ± 0.10	no	no	no
1,4-benzoquinone	1.91 ± 0.10, 1.990 ± 0.048	no	no	no
1,4-dinitrobenzene	2.00 ± 0.10	no <sup>a</sup>	no <sup>a</sup>	no <sup>a</sup>
O <sub>3</sub>	2.103 ± 0.004	yes/no <sup>b</sup>	yes/no <sup>b</sup>	yes/no <sup>b</sup>
NO <sub>2</sub>	2.273 ± 0.005	yes	yes	yes

<sup>a</sup> Electron transfer is observed, but the reaction is slow (i.e.,  $k \sim 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>). <sup>b</sup> Electron transfer is observed, but the reaction rate is unknown.

their electron binding energies (EBEs); the EBE of an anion is equivalent to the electron affinity (EA) of its corresponding neutral species. 3,5-Bis(trifluoromethyl)nitrobenzene (EA = 1.79 ± 0.10 eV) reacts with *o*-benzoquinone radical anion (**4o**) via electron transfer but not with the para isomer, as expected given the known electron affinities of *o*- and *p*-benzoquinone (EA = 1.620 ± 0.048 and 1.91 ± 0.10 or 1.990 ± 0.048 eV, respectively).<sup>20</sup> All three species (**3o**, **3m**, and **3p**) undergo electron transfer with nitrogen dioxide (EA = 2.2730 ± 0.0050 eV), but while this is the sole ionic product with the ortho and para isomers, **3m** also gives oxygen atom transfer (*m*-OC<sub>6</sub>H<sub>4</sub>O<sup>•-</sup>, *m/z* 108) and an adduct (*m*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>O<sup>•-</sup>, *m/z* 138).

Two additional methods for generating **3o** and **3p** were used. Dissociative electron impact on 4-diazo-2,5-cyclohexadienone (6 eV) leads to the loss of molecular nitrogen and formation of an ion that behaves identically to **3p** prepared by CID of *p*-nitrobenzoate (eq 2). We tried to use the same precursor for the formation of **3o**, but the *o*-quinonediazide is difficult to work with and the desired ion can be produced by oxygen-atom transfer to *o*-benzyne radical anion upon reaction with low pressures of carbon dioxide (eq 3). As expected, the reactivity of this ion was found to be identical to **3o** produced from *o*-nitrobenzoate.



**Thermochemistry. Electron Affinities.** The electron binding energies of **3o**, **3m**, and **3p** or equivalently the electron affinities of **1o**, **1m**, and **1p** were determined by reacting these ions with standard reference compounds and observing the occurrence or nonoccurrence of electron transfer. All three radical anions undergo electron transfer upon reaction with 1,4-dinitrobenzene, ozone, and nitrogen dioxide (Table 2). This process does not occur with 1,4-benzoquinone, 3,5-bis(trifluoromethyl)nitrobenzene, and additional compounds with lower electron affinities. These results suggest that the  $\alpha,2-$ ,  $\alpha,3-$ , and  $\alpha,4$ -dehydrophenol radical anions all have the same electron binding energies, and we initially assigned EA(**1o**) = EA(**1m**) = EA(**1p**) = 1.96 ± 0.10 eV.<sup>4b</sup> However, upon closer examination of the data it was

found that the reactions with 1,4-dinitrobenzene are inefficient ( $k \sim 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) and should be considered a “no” in terms of bracketing the electron affinities. Electron transfer also was observed with ozone, but the reaction rates were not determined because of the difficulty in making these measurements. Consequently, the fast reaction ( $\sim 10^{-9}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) with nitrogen dioxide (EA = 2.273 ± 0.005 eV) and the slow process with 1,4-dinitrobenzene (2.00 ± 0.10 eV) are used to assign EA(**1o**) = EA(**1m**) = EA(**1p**) = 2.14 ± 0.17 eV.

To verify our measured electron affinities, a kinetic determination using an approach developed by Squires and co-workers was carried out.<sup>21</sup> The collision-induced dissociation spectra of the conjugate base of 5-nitro-1,3-cyclopentadiene<sup>22</sup> and the radical anions of 2,5-difluoro-1-nitrobenzene and pentafluoronitrobenzene were recorded as a function of pressure ( $\sim 1 \times 10^{-8}$ – $6 \times 10^{-8}$  Torr) and energy.<sup>23</sup> The resulting (*M* – NO<sub>2</sub><sup>-</sup>)/NO<sub>2</sub><sup>-</sup> ratios (*R*) were extrapolated to zero pressure (single collision conditions) and energy (threshold values) and were found to be 0.039 ± 0.018, 0.040 ± 0.005, and 12.3 ± 1.7, respectively. These data were used to construct a calibration line by plotting the known electron binding energies of the *M* – NO<sub>2</sub> anions versus the natural logarithm of *R*,<sup>20</sup> and the following equation was obtained: EA (eV) = 0.223(ln *R*) + 2.62,  $r^2 = 0.96$ . In the exact same way *R* was obtained from *o*-, *m*-, and *p*-nitrophenoxide (*R* = 0.189 ± 0.014, 0.170 ± 0.028, and 0.190 ± 0.018, respectively) to afford EA(**1o**) = EA(**1p**) = 2.25 ± 0.15 eV and EA(**1m**) = 2.23 ± 0.15 eV. These values are in good accord with the bracketing results, are the same as the electron affinity of phenoxy radical (EA = 2.253 ± 0.006 eV)<sup>24a</sup> and, as expected, are much larger than for phenyl radical (EA = 1.096 ± 0.006 eV).<sup>24b</sup> There also is good accord with the MCQDPT2 electron affinities which span a narrow range of 0.1 eV and, after correcting for the error in the computed value for phenoxy radical (10.0 kcal mol<sup>-1</sup>), give predicted electron affinities of 2.39 eV (**1o**), 2.40 eV (**1m**), and 2.28 eV (**1p**) (Table 3). G3, G2+(MP2), and B3LYP calculations were carried out as well on **1o**, **1m**, and **1p** and several well-established reference compounds (Tables 3 and 4) to test these more commonly employed single-configuration approaches. The G3 and B3LYP predictions reproduce the EAs of methoxy, phenoxy, and phenyl radicals to within 2.3 kcal mol<sup>-1</sup>, but the latter results are systematically too small by 1–2 kcal mol<sup>-1</sup>. G2+(MP2) fares less well, missing the EA's of phenoxy and phenyl radicals by 2.9 and 5.2 kcal mol<sup>-1</sup>, respectively. When applied to **1o**, **1m**, and **1p**, the small spread is reasonably reproduced by G3 theory, and all three methods do an adequate job of reproducing the absolute energies, with errors in the ranges of 1–4.5 kcal mol<sup>-1</sup> (G3), 3.7–6.1 kcal mol<sup>-1</sup> (G2+(MP2)), and 1.1–6.1 kcal mol<sup>-1</sup> (B3LYP); the cited values have been corrected for the small computed errors (0.9–2.9 kcal mol<sup>-1</sup>) in the electron affinity of phenoxy radical.

**Proton Affinities.** Proton affinities of **3o**, **3m**, and **3p**, or equivalently the acidity of phenoxy radical at the 2-, 3-, and

- (21) (a) Wenthold, P. G.; Hu, J.; Squires, R. R. *J. Am. Chem. Soc.* **1996**, *118*, 11 865–11 871. (b) Seburg, R. A.; Squires, R. R. *Int. J. Mass Spectrom. Ion Processes* **1997**, *167*, 541–557.
- (22) Methyl nitrate was used instead of ethyl nitrate as this facilitated the procedure and gave better yields (~40% vs 20%). For further details, see: Kerber, R. C.; Chick, M. J. *J. Org. Chem.* **1967**, *32*, 1329–1333.
- (23) These experiments were carried out on a Finnigan FTMS which has been outfitted with an IonSpec OMEGA-2001 data station and vacuum computer.
- (24) (a) Guinion, R. F.; Gilles, M. K.; Polak, M. L.; Lineberger, W. C. *Int. J. Mass Spectrom.* **1992**, *117*, 601–620. (b) Raymond, T. M.; Davico, G. E.; Schwartz, R. L.; Lineberger, W. C. *J. Chem. Phys.* **2000**, *112*, 1158–1169.

**Table 3.** Comparison of Experimental and Directly Computed Proton Affinities, Electron Affinities, and Bond Dissociation Energies for *o*-, *m*-, and *p*-Dehydrophenol Radical Anion (**3o**, **3m**, and **3p**) and Related Species<sup>a</sup>

	B3LYP	G2+(MP2)	G3	MCQDPT2	exptl
EA(X)					
<b>1o</b>	51.6 (53.8)	60.9 (58.0)	53.8 (52.9)	45.0 (55.0)	51.9 ± 3.5
<b>1m<sup>b</sup></b>	55.3 (57.5)	58.4 (55.5)	56.8 (55.9)	45.4 (55.4)	51.4 ± 3.5
<b>1p</b>	48.5 (50.7)	51.1 (48.2)	56.6 (55.7)	42.6 (52.6)	51.9 ± 3.5
PA(X <sup>-</sup> )					
<b>3o</b>					
(C)	374.9	366.7	374.0	368.5	369.4 ± 1.7
(O)	346.5	339.1		337.4	
<b>3m</b>					
(C)	369.9	367.8	369.4	365.1	369.4 ± 1.7
(O)	342.8 [341.2]	342.0 [340.3]		334.1	
<b>3p</b>					
(C)	376.5	374.8 [374.8]	376.1	369.2	369.4 ± 1.7
(O)	347.4 [346.1]	346.6 [345.3]		337.4	
BDE (HX)					
C <sub>6</sub> H <sub>5</sub> O• (C–H)					
ortho	112.9 (114.5)	114.0 (110.6)	114.1 (112.5)	99.8 (114.4)	107.7 ± 3.9
meta <sup>b</sup>	111.5 (113.1)	112.5 (109.1)	113.1 (111.5)	96.9 (111.5)	107.3 ± 3.9
para	111.4 (113.0)	112.2 (108.8)	112.3 (110.7)	98.0 (112.6)	107.7 ± 3.9
C <sub>6</sub> H <sub>5</sub> O <sup>-</sup> (C–H)					
ortho	111.1 (112.8)	108.1 (104.7)	113.3 (111.7)	96.8 (111.4)	107.7 ± 1.0
	[113.2]	[110.2]			
meta	106.1 (107.7)	109.1 (105.7)	108.7 (107.1)	93.3 (107.9)	107.7 ± 1.0
	[107.4]	[110.4]			
para	112.6 (114.3)	116.1 (112.7)	115.4 (113.8)	97.4 (112.0)	107.7 ± 1.0
	[115.8]	[119.2]			
C <sub>6</sub> H <sub>4</sub> OH• (O–H)					
ortho	84.5 (86.1)	86.3 (82.9)		68.7 (83.3)	
	[83.2]	[85.1]			
meta <sup>b</sup>	84.4 (86.0)	86.7 (83.3)		65.9 (80.5)	
	[82.8]	[85.0]			
para	82.4 (84.0)	84.0 (80.6)		66.3 (80.9)	
	[81.1]	[82.8]			

<sup>a</sup> All values in kcal mol<sup>-1</sup>. B3LYP and MCQDPT2 energies are with the 6-311+G(3df,2p) and 6-311+G(d) basis sets, respectively. All energies are ZPE corrected using HF/6-31+G(d), MP2/6-31+G(d) (values in brackets), and MCSCF/6-31G(d) vibrational frequencies. Proton affinities and BDEs also include a temperature adjustment to 298 K. Parenthetical values have been corrected for the error in the appropriate reference compound (see Table 4). <sup>b</sup> G2+(MP2), G3, and B3LYP calculations were carried out using the triplet of  $\alpha$ ,3-dehydrophenol (**1m**). Since this is not the ground state at the MCQDPT2 level, these energies were corrected by the S–T gap (0.6 kcal mol<sup>-1</sup>).

**Table 4.** Comparison of Experimental and Computed Proton Affinities, Electron Affinities, and Bond Dissociation Energies for Reference Compounds<sup>a</sup>

	B3LYP	G2+(MP2)	G3	MCQDPT2	exptl
EA(X•)					
CH <sub>3</sub> O•	34.8	36.9	35.8		36.3 ± 0.1
C <sub>6</sub> H <sub>5</sub> O•	49.8 [52.9]	54.9 [58.1]	52.9	42.0	52.0 ± 0.1
C <sub>6</sub> H <sub>5</sub> •	23.8 [28.1]	30.5 [34.8]	27.6	14.9	25.3 ± 0.1
absolute mean error (max error)	1.7(-2.2)	2.9(5.2)	1.2(2.3)	10.2(10.4)	
PA(X <sup>-</sup> )					
CH <sub>3</sub> O <sup>-</sup>	380.9	383.0	383.6		382.4 ± 0.5
C <sub>6</sub> H <sub>5</sub> O <sup>-</sup>	348.1	348.6	349.5	340.5	350.4 ± 0.6
C <sub>6</sub> H <sub>5</sub> <sup>-</sup>	401.7	400.0	401.3	397.8	401.7 ± 0.5
absolute mean error (max error)	1.3(2.3)	1.0(1.8)	0.8(1.2)	6.9(9.9)	
BDE(HX)					
CH <sub>3</sub> OH	101.9	106.3	106.0		105.2 ± 0.7
C <sub>6</sub> H <sub>5</sub> OH	84.2 [86.9]	89.9 [92.6]	88.9	68.7 <sup>b</sup>	88.8 ± 0.6
C <sub>6</sub> H <sub>5</sub> H	111.9 [116.0]	116.9 [120.9]	115.1	98.9 <sup>b</sup>	113.5 ± 0.5
absolute mean error (max error)	3.2(4.6)	1.9(3.4)	0.8(1.6)	17.4(20.1)	

<sup>a</sup> All values in kcal mol<sup>-1</sup> and include a ZPE correction using HF/6-31+G(d), MP2/6-31+G(d) (values in brackets) or MCSCF vibrational frequencies. Proton affinities and BDEs are at 298 K. B3LYP and MCQDPT2 energies are with the 6-311+G(3df,2p) and 6-311+G(d) basis sets, respectively. <sup>b</sup> The C<sub>6</sub>H<sub>5</sub>O–H and C<sub>6</sub>H<sub>5</sub>–H bond energies increase by 8.5 and 8.9 kcal mol<sup>-1</sup>, respectively, if the ZPEs are omitted.

4-positions, also were examined by the bracketing method. Proton transfer was observed between all three radical anions and the *N,N*-dimethylamide of propiolic acid ((CH<sub>3</sub>)<sub>2</sub>NCOC≡CH) and stronger acids, but not with *p*-fluoroaniline, acetone, *N,N*-diethylhydroxylamine, phenylacetylene, and weaker species (Table 5). Hydrogen atom abstraction takes place as well with many of the reference acids (HX) that were employed, and this competing pathway could result in the failure to observe X<sup>-</sup>

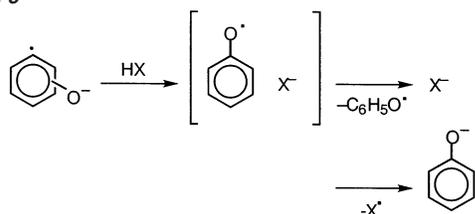
when proton transfer is an exothermic process. This complication arises because phenoxyl radical has a large electron affinity, which in most cases is greater than the value for X•. As a result, the [C<sub>6</sub>H<sub>5</sub>O• X<sup>-</sup>] complex formed upon proton transfer probably is better described as [C<sub>6</sub>H<sub>5</sub>O<sup>-</sup> X•] and preferentially dissociates to phenoxide ion and X• rather than phenoxyl radical and X<sup>-</sup> (Scheme 3). This potential problem can be addressed by using reference acids whose conjugate bases have electron affinities

**Table 5.** Proton Affinity Bracketing Results for **3o**, **3m**, and **3p**<sup>a</sup>

reagent	$\Delta H_{\text{acid}}^{\circ}$	BDE	<b>3o</b>		<b>3m</b>		<b>3p</b>	
			PT	HT	PT	HT	PT	HT
NH <sub>3</sub>	404.3 ± 0.3	108.5 ± 0.3	no	no	no	no	no	no
C <sub>6</sub> D <sub>6</sub> <sup>b</sup>	401.7 ± 0.5	113.5 ± 0.5	no	no	no	no	no	no
D <sub>2</sub> O	393.0 ± 0.2	121.4 ± 0.2	no	no	no	no	no	no
CH <sub>3</sub> OH	382.4 ± 0.5	105.2 ± 0.7	no	yes	no	yes	no	yes
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	382.3 ± 0.5	89.8 ± 0.6	no	no	no	no	no	no
CH <sub>3</sub> CH <sub>2</sub> OH	379.1 ± 1.2	105.4 ± 1.4	no	yes	no	yes	no	yes
(CH <sub>3</sub> ) <sub>3</sub> COH	376.4 ± 0.7	106.8 ± 1.0	no	yes	no	yes	no	yes
CH <sub>3</sub> CN	372.9 ± 2.1	94.8 ± 2.1	no	yes	no	yes	no	yes
HF	371.6 ± 0.2	136.4 ± 0.2	no	no	no	no	no	no
C <sub>6</sub> H <sub>5</sub> C≡CH	370.6 ± 2.3	133 ± 5	no	no	no	no	no	no
(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NOH	370.6 ± 2.1	69.6 ± 1.9	no	yes	no	yes	no	yes
CH <sub>3</sub> COCH <sub>3</sub>	369.1 ± 2.1	96.0 ± 2.2	no	yes	no	yes	no	yes
<i>p</i> -FC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	364.3 ± 2.1	92.9 ± 2.1	no	yes	no	yes	no	yes
(CH <sub>3</sub> ) <sub>2</sub> NCOC≡CH	362.5 ± 2.1	132 ± 5	yes	no	yes	no	yes	no
CF <sub>3</sub> CH <sub>2</sub> OH	361.7 ± 2.5	107.0 ± 2.5	yes	yes	yes	yes	yes	yes
HC≡CCO <sub>2</sub> CH <sub>3</sub>	358.7 ± 2.1	132 ± 5	yes	no	yes	no	yes	no
(CH <sub>3</sub> ) <sub>3</sub> CSH	352.5 ± 2.2	86.6 ± 2.2	yes	yes	yes	yes	yes	yes

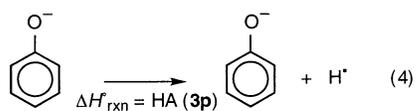
<sup>a</sup> All values in kcal mol<sup>-1</sup>. PT = proton transfer and HT = hydrogen atom transfer. <sup>b</sup> Values for the protio compound are given. <sup>c</sup> A trace of proton-transfer product was observed, but this result was not reproducible.

**Scheme 3**



in excess of 2.3 eV (e.g., HF and acetylene derivatives). Consequently, we used (CH<sub>3</sub>)<sub>2</sub>NCOC≡CH ( $\Delta H_{\text{acid}}^{\circ} = 362.5 \pm 2.1$  kcal/mol) and PhC≡CH ( $\Delta H_{\text{acid}}^{\circ} = 370.7 \pm 2.3$  kcal/mol) as our brackets and assign PA(**3o**, **3m**, and **3p**) ≥ 367 ± 5 kcal/mol. These values are assigned as lower numerical limits because proton transfer to **3o**, **3m**, and **3p** is apt to have a kinetic barrier; C-protonation is thermodynamically favored, but the bulk of the charge is on the more electronegative (and less basic) oxygen atom.

To derive the heats of formation of the three oxocyclohexadienylidenes (**1o**, **1m**, and **1p**) from our data, we need to use the proton affinities of **3o**, **3m**, and **3p**. Fortunately, these quantities could be determined more precisely by bracketing the hydrogen-atom affinity (HA) of **3o**, **3m**, and **3p** (eq 4) and making use of the thermodynamic cycle shown in eq 5. All three dehydrophenol radical anions undergo hydrogen atom abstraction with the majority of reagents that were examined, and all of the alcohols (MeOH, EtOH, *tert*-BuOH, and CF<sub>3</sub>-CH<sub>2</sub>OH) listed in Table 5. To determine the abstraction site in



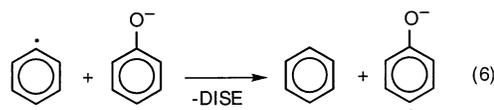
$$\text{PA}(\mathbf{3p}) = \text{HA}(\mathbf{3p}) + \text{IP}(\text{H}^+) - \text{EA}(\text{PhO}^-) \quad (5)$$

the latter compounds (C vs O), **3o**, **3m**, and **3p** were reacted with deuterated (ROD) alcohols. In each case, hydrogen and deuterium atom transfer was observed in approximately a statistical (nonselective) fashion. These results indicate that the

ortho, meta, and para C–H bond dissociation energies of phenoxide ion are greater than the O–H bond strengths of methanol (105.2 ± 0.7 kcal mol<sup>-1</sup>), ethanol (105.4 ± 1.4 kcal mol<sup>-1</sup>), *tert*-butyl alcohol (106.8 ± 1.0 kcal/mol), and 2,2,2-trifluoroethanol (107.0 ± 2.5 kcal mol<sup>-1</sup>).<sup>20,24b</sup> Ammonia, benzene, and deuterium oxide (BDEs = 108.5 ± 0.3, 113.5 ± 0.5, and 121.4 ± 0.2 kcal/mol, respectively),<sup>25</sup> on the other hand, do not undergo hydrogen or deuterium atom abstraction with **3o**, **3m**, and **3p**, so we assign HA(**3o**, **3m**, and **3p**) = 107.7 ± 1.7 kcal/mol. These values are in reasonable accord with MCQDPT2 predictions of 111.4 (**3o**), 107.9 (**3m**), and 112.0 (**3p**) kcal mol<sup>-1</sup> after correcting for the 14.6 kcal mol<sup>-1</sup> error in the C–H BDE for benzene (Table 3). Alternatively, the directly computed non-ZPE corrected 0 K bond energies are 105.2, 101.9, and 105.8 kcal mol<sup>-1</sup>, respectively. This latter approach is consistent with Wiberg's finding that hydrocarbon BDEs are well reproduced at the MP2 level if ZPE corrections are omitted.<sup>26</sup> As for the G3, G2+(MP2), and B3LYP calculations, they do a better job reproducing the C–H bond strength for benzene and are in good accord with our experimental results for **3o** and **3m**; the computed bond energy for **3p** is consistently somewhat too strong.

By combining the measured hydrogen atom affinities with the known electron affinity of phenoxyl radical (51.95 ± 0.14 kcal mol<sup>-1</sup>) and the ionization potential of hydrogen atom (313.6 kcal mol<sup>-1</sup>, eq 5), we obtain PA(**3o**, **3m**, and **3p**) = 369.4 ± 1.7 kcal mol<sup>-1</sup>. These values are in accord with the bracketing results for these anions (≥ 367 ± 5 kcal mol<sup>-1</sup>) and are in good agreement with MCQDP2 predictions of 368.5 (**3o**), 365.1 (**3m**), and 369.2 (**3p**) kcal mol<sup>-1</sup>. The G2+(MP2) results also are in good accord with experiment for **3o** (366.7 kcal mol<sup>-1</sup>) and **3m** (367.8 kcal mol<sup>-1</sup>) but not **3p** (374.8 kcal mol<sup>-1</sup>). As for the G3 and B3LYP proton affinities, they reproduce the value for the α,3-isomer but give poor values for the α,2- and α,4-species (Table 3).

**Heats of Formation.** Our thermochemical data on the α,2-, α,3-, and α,4-dehydrophenol radical anions can now be used to derive their heats of formation and those for the corresponding oxocyclohexadienylidenes **1o**, **1m**, and **1p**. Taking the former quantities first, one can combine the known heat of formation of phenoxide ion (−38.3 ± 0.6 kcal mol<sup>-1</sup>, Table 6) with the measured hydrogen atom affinities of **3o**, **3m**, and **3p** to derive  $\Delta H_{\text{f}}^{\circ}(\mathbf{3o}, \mathbf{3m}, \text{and } \mathbf{3p}) = 17.3 \pm 1.8$  kcal mol<sup>-1</sup>. To put this quantity in perspective, we consider the isodesmic reaction illustrated in eq 6, which we term the distonic ion separation



energy (DISE). This proposal is directly modeled on the bi-radical separation energy (BSE, see below) originally described by Wenthold et al.<sup>27</sup> The DISE provides a correction to bond

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- (26) Wiberg, K. B.; Hadad, C. M.; Sieber, S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 5820–5828.
- (27) Wenthold, P. G.; Wierschke, S. G.; Nash, J. J.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 7378–7392.

**Table 6.** Ancillary Thermochemical Data Used and Generated in This Work<sup>a</sup>

$\Delta H_{\text{f}}^{\circ}(\text{C}_6\text{H}_6) = 19.82 \pm 0.12$	$\text{BDE}(\text{C}_6\text{H}_5\text{-H}) = 113.5 \pm 0.5$	$\Delta H_{\text{acid}}^{\circ}(\text{C}_6\text{H}_6) = 401.7 \pm 0.5$
$\text{EA}(\text{C}_6\text{H}_5^{\bullet}) = 25.3 \pm 0.1$	$\Delta H_{\text{f}}^{\circ}(\text{C}_6\text{H}_5^{\bullet}) = 55.8 \pm 0.5$	$\Delta H_{\text{f}}^{\circ}(\text{C}_6\text{H}_5^{\bullet}) = 81.2 \pm 0.6$
$\Delta H_{\text{f}}^{\circ}(\text{C}_6\text{H}_5\text{OH}) = -23.03 \pm 0.13$	$\text{BDE}(\text{C}_6\text{H}_5\text{O-H}) = 88.8 \pm 0.6$	$\Delta H_{\text{acid}}^{\circ}(\text{C}_6\text{H}_5\text{OH}) = 350.4 \pm 0.6$
$\text{EA}(\text{C}_6\text{H}_5\text{O}^{\bullet}) = 51.95 \pm 0.14$	$\Delta H_{\text{f}}^{\circ}(\text{C}_6\text{H}_5\text{O}^{\bullet}) = -38.3 \pm 0.6$	$\Delta H_{\text{f}}^{\circ}(\text{C}_6\text{H}_5\text{O}^{\bullet}) = 13.7 \pm 0.6$

<sup>a</sup> All values come from refs 20, 24, and 25.

**Table 7.** Distonic Ion Separation Energies and Heats of Formation of the  $\alpha$ ,2-,  $\alpha$ ,3-, and  $\alpha$ ,4-Dehydrophenol Radical Anions

method	DISE, kcal mol <sup>-1</sup>			$\Delta H_{\text{f}}^{\circ}$ , kcal mol <sup>-1</sup>		
	$\alpha$ ,2	$\alpha$ ,3	$\alpha$ ,4	$\alpha$ ,2	$\alpha$ ,3	$\alpha$ ,4
B3LYP	0.8 [2.8]	5.8 [8.6]	-0.7 [0.2]	22.3 [20.3]	17.3 [14.5]	23.8 [22.9]
G2+(MP2)	8.8 [10.7]	7.8 [10.5]	0.8 [1.7]	14.3 [12.4]	15.3 [12.3]	22.3 [21.4]
G3	1.8	6.4	-0.3	21.3	16.7	23.4
MCSCF	0.2	3.1	-0.7	23.0	20.1	23.9
MCQDPT2	2.1	5.6	1.5	21.1	17.6	21.7
exptl	5.8 $\pm$ 1.8	5.8 $\pm$ 1.8	5.8 $\pm$ 1.8	17.3 $\pm$ 1.8	17.3 $\pm$ 1.8	17.3 $\pm$ 1.8

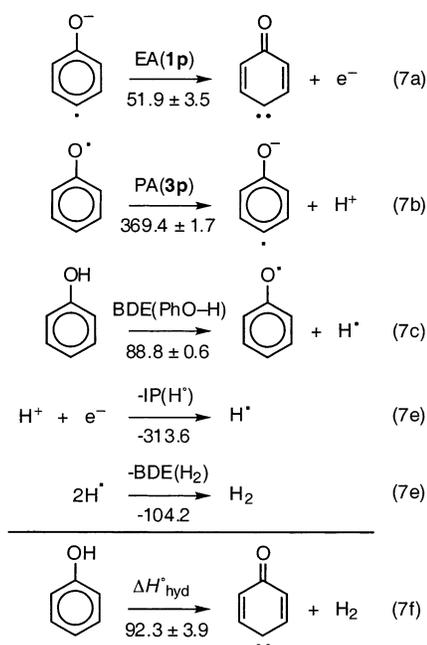
**Table 8.** Biradical Separation Energies and Heats of Formation of  $\alpha$ ,2-,  $\alpha$ ,3-, and  $\alpha$ ,4-Dehydrophenol

method	BSE, kcal mol <sup>-1</sup>			$\Delta H_{\text{f}}^{\circ}$ , kcal mol <sup>-1</sup>		
	$\alpha$ ,2	$\alpha$ ,3	$\alpha$ ,4	$\alpha$ ,2	$\alpha$ ,3	$\alpha$ ,4
B3LYP	-1.0 [3.1]	0.4 [4.5]	0.5 [4.6]	76.1 [72.0]	74.7 [70.6]	74.6 [70.5]
G2+(MP2)	2.9 [6.9]	4.4 [8.4]	4.7 [8.7]	72.2 [68.2]	70.7 [66.7]	70.4 [66.4]
G3	1.0	2.0	2.8	74.1	73.1	72.3
MCSCF	0.7	3.6	2.9	74.5	71.6	72.3
MCQDPT2	-0.9	2.0	0.9	76.1	73.2	74.3
exptl.	5.8 $\pm$ 4.0	5.4 $\pm$ 4.0	5.8 $\pm$ 4.0	69.3 $\pm$ 3.9	68.9 $\pm$ 3.9	69.3 $\pm$ 3.9

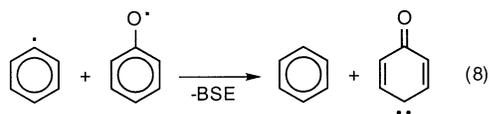
additivity by providing a measure of the stabilizing or destabilizing interaction of a charged center with a radical center in a given molecule. If there is mutual stabilization the DISE will be a positive number, and if the two centers destabilize each other then the DISE will be a negative number. In the case illustrated in eq 6, the DISE is equivalent to  $\text{BDE}(\text{C}_6\text{H}_5\text{-H}) + \text{IP}(\text{H}^{\bullet}) - \text{EA}(\text{C}_6\text{H}_5\text{O}^{\bullet}) - \text{PA}(p\text{-C}_6\text{H}_4\text{O}^{\bullet-})$  or  $375.2 \pm 0.5$  kcal mol<sup>-1</sup> -  $\text{PA}(p\text{-C}_6\text{H}_4\text{O}^{\bullet-})$ . The same relationship holds for the  $\alpha$ ,2- and  $\alpha$ ,3-isomers, and thus the DISEs for all three  $\alpha$ ,*n*-dehydrophenol radical anions are  $5.8 \pm 1.8$  kcal mol<sup>-1</sup>. This means that there is a slight stabilizing interaction between the charged and radical centers, and consequently the carbon-hydrogen BDE of benzene is somewhat larger than any of the C-H bonds in phenoxide ion. This result is in keeping with Wenthold et al., who found that the  $\sigma$ - $\pi$  exchange energy is worth about 4–5 kcal mol<sup>-1</sup> in these type of systems.<sup>27</sup> All of the computational procedures that were examined reproduce the DISE for the  $\alpha$ ,3-isomer but are somewhat too small for the other two isomers (Table 7). In any case, the calculated DISEs can be combined with the known heats of formation of benzene, phenyl radical, and phenoxide to predict the heats of formation of **3o**, **3m**, and **3p**. The resulting MCQDPT2 energies only span a 4 kcal mol<sup>-1</sup> range (17.6 (**3m**), 21.1 (**3o**), and 21.7 (**3p**) kcal mol<sup>-1</sup>) and are in reasonable accord with our experimental findings. Similar results also are obtained at the G3, G2+(MP2), and B3LYP levels.

The heats of hydrogenation of oxocyclohexadienylenes **1o**, **1m**, and **1p** can be derived from our data by combining the electron affinities of **1o**, **1m**, and **1p**, the proton affinities of **3o**, **3m**, and **3p**, the ionization potential of hydrogen atom, the bond dissociation energy (BDE) of molecular hydrogen, and the O-H BDE of phenol in a thermodynamic cycle as

illustrated for  $\alpha$ ,4-dehydrophenol (eq 7, all values in kcal mol<sup>-1</sup>).



These quantities ( $92.3 \pm 3.9$  kcal mol<sup>-1</sup> for **1o** and **1p** and  $91.9 \pm 3.9$  kcal mol<sup>-1</sup> for **1m**) when combined with the known heat of formation of phenol ( $-23.03 \pm 0.13$  kcal/mol) lead to  $\Delta H_{\text{f}}^{\circ}(\mathbf{1o}$  and  $\mathbf{1p}) = 69.3 \pm 3.9$  kcal mol<sup>-1</sup> and  $\Delta H_{\text{f}}^{\circ}(\mathbf{1m}) = 68.9 \pm 3.9$  kcal mol<sup>-1</sup> (Table 8). These values are the same within the experimental uncertainties and are  $\sim 6$  kcal mol<sup>-1</sup> less than predicted by additivity. In other words, the biradical separation energy is 5–6 kcal mol<sup>-1</sup> for **1o**, **1m**, and **1p** (eq 8).



Our findings are analogous to those reported by Wenthold et al. for the  $\alpha,n$ -dehydrotoluenes (i.e., they have the same heats of formation and they are 5 kcal mol<sup>-1</sup> less than predicted by bond additivity) and are in reasonable accord with theory.<sup>28</sup> It is also worth noting that Wenthold et al. measured the heats of formation of **1o** and **1p** by a totally independent technique (energy-resolved collision-induced dissociation) and obtained 69–70 kcal mol<sup>-1</sup> for **1o** and **1p**, which is in very good agreement with our results; the CID method failed for **1m**, presumably because a rearrangement occurred.<sup>29,30</sup>

Based upon our data, the C–H bond energies of phenoxy radical can be derived (Table 3). In addition, by using the calculated energy difference between 1*H*-bicyclo[3.1.0]hexa-3,5-dien-2-one (**1b**) and **1p** reported by Sole et al.,<sup>4a</sup> we estimate that  $\Delta H_f^\circ(\mathbf{1b}) = 88$  kcal mol<sup>-1</sup>. This quantity is  $\sim 30$  kcal mol<sup>-1</sup> larger than a previously reported value (57 kcal mol<sup>-1</sup>) based upon MP2 calculations.<sup>3e</sup> The smaller prediction must be incorrect since the measured heat of formation of **1p** (69 kcal mol<sup>-1</sup>) is larger and **5** is known to thermally isomerize to **1p** at 35 K. Presumably, MP2 fails in this case because **5** requires more than a one configuration wave function to be adequately described.

## Conclusions

Sequential fragmentation of carbon dioxide and nitric oxide from *o*-, *m*-, and *p*-nitrobenzoate affords the  $\alpha,2$ -,  $\alpha,3$ -, and  $\alpha,4$ -

dehydrophenoxide anions (**3o**, **3m**, and **3p**). The  $\alpha,2$ - and  $\alpha,4$ -isomers were independently prepared from *o*-benzyne radical anion and *p*-diazophenol, respectively, and the structures of all three isomers were rigorously established (i.e., **3o**, **3m**, and **3p** have different reactivities, they all were converted to phenoxide and their corresponding quinones, and these derivatives were found to be identical to the authentic species). Electron affinities, proton affinities, and hydrogen atom affinities were measured by bracketing, and in the first case, a kinetic technique also was used. The results are in reasonable accord with MCQDPT2, G3, G2+(MP2), and B3LYP calculations and were combined in thermodynamic cycles to afford the heats of formation of **3o**, **3m**, and **3p** and their corresponding  $\alpha,n$ -dehydrophenols. In both cases, the energies of the three isomers are the same, and they are more stable than predicted by bond additivity by 5–6 kcal mol<sup>-1</sup>. These results are analogous to Wenthold and Squire's earlier work on  $\alpha,n$ -dehydrotoluenes and can be attributed to the  $\sigma$ – $\pi$  exchange energy. Our data also suggests that 1*H*-bicyclo[3.1.0]hexa-3,5-dien-2-one (**1b**) is  $\sim 30$  kcal mol<sup>-1</sup> less stable than previously suggested.

**Acknowledgment.** We thank Prof. Paul Wenthold for kindly sharing unpublished data on the  $\alpha,n$ -dehydrophenols and Dr. Lev Lis for providing a sample of 5-nitro-1,3-cyclopentadiene. Support from the National Science Foundation, the donors of the Petroleum Research Foundation, as administered by the American Chemical Society, the Air Force Office of Scientific Research, and the Minnesota Supercomputer Institute are gratefully acknowledged. G.C. thanks the Korea Science and Engineering Foundation for financial support (Grant No. R05-2000-000-00060-0 (2002)).

JA029571C

(28) For a detailed discussion relating to the computational shortcomings of  $\sigma,\pi$  biradicals and BSEs, see ref 27.

(29) Wenthold, P. G. Ph.D. Thesis, Purdue University, 1994.

(30) Wenthold, P. G.; Nash, J. J.; Hill, B. T.; Squires, R. R., unpublished work.