J. Phys. Chem. A **2007,** *111,* 8741−8748

Energetics of Cresols and of Methylphenoxyl Radicals

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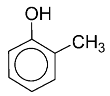
Received: May 8, 2007; In Final Form: June 27, 2007

Combustion calorimetry studies were used to determine the standard molar enthalpies of formation of *o*-, *m*-, and *p*-cresols, at 298.15 K, in the condensed state as $\Delta_f H_m°(o\text{-}CH_3C_6H_4OH,cr) = -204.2 \pm 2.7$ kJ·mol^{-1}, $\Delta_f H_m°(m\text{-}CH_3C_6H_4OH,l) = -196.6 \pm 2.1$ kJ·mol^{-1}, and $\Delta_f H_m°(p\text{-}CH_3C_6H_4OH,cr) = -202.2 \pm 3.0$ kJ·mol^{-1}. Calvet drop calorimetric measurements led to the following enthalpy of sublimation and vaporization values at 298.15 K: $\Delta_{sub} H_m°(o\text{-}CH_3C_6H_4OH) = 73.74 \pm 0.46$ kJ·mol^{-1}, $\Delta_{vap} H_m°(m\text{-}CH_3C_6H_4OH) = 64.96 \pm 0.69$ kJ·mol^{-1}, and $\Delta_{sub} H_m°(p\text{-}CH_3C_6H_4OH) = 73.13 \pm 0.56$ kJ·mol^{-1}. From the obtained $\Delta_f H_m°$(l/cr) and $\Delta_{vap} H_m°/\Delta_{sub} H_m°$ values, it was possible to derive $\Delta_f H_m°(o\text{-}CH_3C_6H_4OH,g) = -130.5 \pm 2.7$ kJ·mol^{-1}, $\Delta_f H_m°(m\text{-}CH_3C_6H_4OH,g) = -131.6 \pm 2.2$ kJ·mol^{-1}, and $\Delta_f H_m°(p\text{-}CH_3C_6H_4OH,g) = -129.1 \pm 3.1$ kJ·mol^{-1}. These values, together with the enthalpies of isodesmic and isogyric gas-phase reactions predicted by the B3LYP/cc-pVDZ, B3LYP/cc-pVTZ, B3P86/cc-pVDZ, B3P86/cc-pVTZ, MPW1PW91/cc-pVTZ, CBS-QB3, and CCSD/cc-pVDZ//B3LYP/cc-pVTZ methods, were used to obtain the differences between the enthalpy of formation of the phenoxyl radical and the enthalpies of formation of the three methylphenoxyl radicals: $\Delta_f H_m°(C_6H_5O^\bullet,g) - \Delta_f H_m°(o\text{-}CH_3C_6H_4O^\bullet,g) = 42.2 \pm 2.8$ kJ·mol^{-1}, $\Delta_f H_m°(C_6H_5O^\bullet,g) - \Delta_f H_m°(m\text{-}CH_3C_6H_4O^\bullet,g) = 36.1 \pm 2.4$ kJ·mol^{-1}, and $\Delta_f H_m°(C_6H_5O^\bullet,g) - \Delta_f H_m°(p\text{-}CH_3C_6H_4O^\bullet,g) = 38.6 \pm 3.2$ kJ·mol^{-1}. The corresponding differences in O−H bond dissociation enthalpies were also derived as $DH°(C_6H_5O{-}H) - DH°(o\text{-}CH_3C_6H_4O{-}H) = 8.1 \pm 4.0$ kJ·mol^{-1}, $DH°(C_6H_5O{-}H) - DH°(m\text{-}CH_3C_6H_4O{-}H) = 0.9 \pm 3.4$ kJ·mol^{-1}, and $DH°(C_6H_5O{-}H) - DH°(p\text{-}CH_3C_6H_4O{-}H) = 5.9 \pm 4.5$ kJ·mol^{-1}. Based on the differences in Gibbs energies of formation obtained from the enthalpic data mentioned above and from published or calculated entropy values, it is concluded that the relative stability of the cresols varies according to *p*-cresol < *m*-cresol < *o*-cresol, and that of the radicals follows the trend *m*-methylphenoxyl < *p*-methylphenoxyl < *o*-methylphenoxyl. It is also found that these tendencies are enthalpically controlled.

Introduction

The three isomers of methylphenol (**1**, **2**, and **3**), commonly dubbed cresols, are important materials in the production of resins, polymers, antiseptics, antioxidants, and a variety of other chemicals used for agricultural, cosmetic, and pharmaceutical applications.[1,2] Their energetics are also implicated in many fundamental studies, such as the relationships of enthalpy of formation[3] and O−H bond dissociation enthalpies, $DH°$(O−H),[4,5] with the molecular structure, the antioxidant activity of phenol derivatives,[4−6] the depolymerization of coal,[7,8] and the fate of atmospheric pollutants released to the environment.[9,10]



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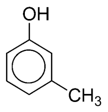

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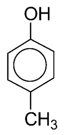

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It is therefore surprising that some significant discrepancies are found between the published enthalpies of formation, enthalpies of vaporization/sublimation, and $DH°$(O−H) values of cresols. Even excluding early results that are only of historical value,[11−14] it is possible to conclude that the published enthalpies of formation of *o*-cresol (cr), *m*-cresol (l), and *p*-cresol (cr), at 298.15 K, span ranges of 2.6 kJ·mol^{-1},[15−18] 17.0 kJ·mol^{-1},[15−19] and 6.3 kJ·mol^{-1},[15−18] respectively. The enthalpies of sublimation of both *o*-cresol and *p*-cresol at 298.15 K have been determined only once,[16,20] and the reported values of the enthalpy of vaporization of *m*-cresol at 298.15 K vary between 46.3 and 71.2 kJ·mol^{-1}.[16,20−25] To our knowledge, no direct measurements of the gas phase O−H bond dissociation enthalpies of cresols exist. The available values are derived from correlations based on electrochemical and pK_a determinations,[26−31] kinetic[32] and equilibrium[33] studies in solution, quantum chemistry calculations,[34−37] and gas phase acidity measurements combined with calculated electron affinities.[38] The recommended value ranges are 351−369 kJ·mol^{-1} (*o*-cresol),[28,34] 351−377 kJ·mol^{-1} (*m*-cresol),[28,29,34,38] and 350−397 kJ·mol^{-1} (*p*-cresol).[26−37] These discrepancies may, at least in part, result from the different anchors and assumptions used by the authors, since much better agreement is obtained when the differences

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10.1021/jp073515m CCC: $37.00

between the O−H bond dissociation enthalpies in phenol and in the cresols are considered. Fortunately, only the values of these differences, rather than the absolute $DH°$(O−H) values, are required to address questions such as the relative thermodynamic stabilities and the antioxidant activities of phenolic compounds.[4] The origins of the inconsistencies in the enthalpies of formation and vaporization/sublimation are difficult to ascertain, and this led us to redetermine $\Delta_f H_m°$(l,cr) and $\Delta_{vap}H_m°/\Delta_{sub}H_m°$ for the three isomers of cresol by using combustion and Calvet drop calorimetry. The obtained results were then used to derive the corresponding $\Delta_f H_m°$(g) values, which together with theoretical predictions for the enthalpies of selected isodesmic and isogyric reactions, enabled the derivation of $DH°(C_6H_5O{-}H) - DH°(MeC_6H_4O{-}H)$ values, and a discussion of the relative thermodynamic stabilities of the three cresol isomers and of the corresponding methylphenoxyl radicals.

Experimental Section

General. The cresol samples were handled under an oxygen and water free (<5 ppm) nitrogen atmosphere inside a glovebox, or using standard Schlenk techniques. Infrared spectra (FT-IR) were obtained with a Brüker Tensor 27 Fourier transform spectrophotometer calibrated with polystyrene film. The samples were mounted as Nujol mulls between CsI plates inside the glovebox. The ^{1}H NMR spectra were recorded at ambient temperature, in C_6D_6 (Aldrich 99.6%), on a Varian Unity Inova 300 MHz spectrometer. Gas chromatography (GC) experiments were performed on a Shimatzu 9A apparatus coupled to a flame ionization detector (FID), using a Carbopack (80/100 mesh; C/0.1% SP-1000) column. The carrier gas was helium at a flow of 0.42 $cm^3 \cdot s^{-1}$. The temperature of the injector was set at 523 K and the oven temperature was programmed as follows: run 1, 348 K (5 min), ramp at 10 $K \cdot min^{-1}$, 498 K (60 min); run 2, 498 K (isothermal, 90 min). Binary and ternary mixtures of the different cresols were also injected to confirm the effective separation of the three isomers under the experimental conditions used in runs 1 and 2.

The differential scanning calorimetry (DSC) experiments were made with a temperature-modulated TA Instruments Inc. 2920 MTDSC apparatus, operated as a conventional DSC. The samples with masses in the range 4.8−25.6 mg were sealed in aluminum pans under N_2 atmosphere inside a glovebox, and weighed with a precision of 10^{-7} g in a Mettler UMT2 ultramicrobalance. Helium (Air Liquide N55), at a flow rate of 0.5 $cm^3 \cdot s^{-1}$, was used as the purging gas. The temperature and heat flow scales of the instrument were calibrated as previously described.[39] The heating rate used in the experiments was 5 $K \cdot min^{-1}$.

Materials. *o*-Cresol (Aldrich, 99%) and *m*-cresol (Aldrich, 99%) were distilled under nitrogen atmosphere (1 bar) at 463 and 475 K, respectively. *p*-Cresol (Aldrich, 99%) was sublimed in a vacuum (6.7 Pa) at 298 K. The purified samples were kept in the glovebox prior to the calorimetric experiments.

^{1}H NMR for *o*-C_7H_8O (300 MHz, C_6D_6/TMS): $\delta = 7.04$ (s, 1H), 7.02 (s, 1H), 6.49 (s, 1H), 4.58 (s, 1H) 2.15 (s, 1H). FT-IR (main peaks), ν/cm^{-1}: 3423 (st, O−H); 1592, 1464 (st C−C ring); 1328 (in-plane bd, O−H); 1259 (st, C−O); 752 (out-of-plane bd, C−H). The GC analysis indicated that the purity of the sample was 99.99%. ^{1}H NMR for *m*-C_7H_8O (300 MHz, C_6D_6/TMS): $\delta = 6.96$ (s, 1H), 6.59 (s, 1H), 6.42 (s, 1H), 4.50 (s, 1H) 2.01 (s, 1H). FT-IR (main peaks), ν/cm^{-1}: 3356 (st, O−H); 1591, 1460 (st C−C ring); 1377 (in-plane bd, O−H); 1262 (st, C−O); 776 (out-of-plane bd, C−H). The GC analysis indicated that the purity of the sample was 99.99%. ^{1}H NMR for *p*-C_7H_8O (300 MHz, C_6D_6/TMS): $\delta = 6.8$ (d, 2H), 6.4 (d, 2H), 3.8 (s, 1H), 2.0 (s, 3H). FT-IR (main peaks), ν/cm^{-1}: 3331 (st, O−H); 1598, 1514, 1461 (st C−C ring); 1377 (in-plane bd, O−H); 1257 (st, C−O); 815 (out-of-plane bd, C−H). The GC analysis indicated that the purity of the sample was 99.99%.

The absence of water in all samples was confirmed by the nonexistence of the H−O−H bending frequency at 1644 cm^{-1} in the FT-IR spectra.

The onset, T_{on}, and maximum, T_{max}, temperatures of the fusion peaks obtained by DSC were $T_{on} = 302.2 \pm 0.4$ K and $T_{max} = 305.4 \pm 0.2$ K for *o*-cresol, $T_{on} = 278.2 \pm 0.2$ K and $T_{max} = 282.3 \pm 0.2$ K for *m*-cresol, and $T_{on} = 307.3 \pm 0.3$ K and $T_{max} = 308.8 \pm 0.1$ K for *p*-cresol. These values are in good agreement with the reported fusion temperatures of 304.14 ± 0.01 K[16] and 304.1 ± 0.3 K[40] (*o*-cresol), 285.37 ± 0.02 K[16] and 280.8 ± 0.2 K[40] (*m*-cresol), and 307.84 ± 0.02 K[16] and 307.4 ± 0.1 K[40] (*p*-cresol). The DSC analysis also led to the following enthalpies of fusion at the fusion temperatures mentioned above: $\Delta_{fus}H_m°(o\text{-}CH_3C_6H_4OH) = 14.8 \pm 0.1$ kJ·mol^{-1}, $\Delta_{fus}H_m°(m\text{-}CH_3C_6H_4OH) = 8.9 \pm 0.1$ kJ·mol^{-1}, and $\Delta_{fus}H_m°(p\text{-}CH_3C_6H_4OH) = 12.6 \pm 0.1$ kJ·mol^{-1}. These results are similar to the corresponding values found in the literature, which range from 13.9 to 15.8 kJ·mol^{-1} (*o*-cresol), from 9.1 to 10.7 kJ·mol^{-1} (*m*-cresol), and from 11.8 to 12.7 kJ·mol^{-1} (*p*-cresol), respectively.[41] The uncertainties quoted above for the T_{on}, T_{max}, and $\Delta_{fus}H_m°$ obtained in this work correspond to twice the standard deviation of the mean of five independent determinations.

No phase transitions other than fusion were observed in the DSC curves of the *o*- and *p*-cresol samples used in the combustion and sublimation experiments. The lowest temperatures of the ranges covered by the experiments were 250 K in the first case and 220 K in the second case. The *m*-cresol isomer with $T_{on} = 307.3 \pm 0.3$ K is liquid at the temperature of the combustion and vaporization experiments (298.15 K).

Combustion Calorimetry. The isoperibol static-bomb combustion calorimeter used in the determination of the enthalpies of formation of *o*-, *m*-, and *p*-cresols has been described.[42] The energy equivalent of the calorimeter, $\epsilon° = 18\,566.08 \pm 2.87$ J·K^{-1}, was determined in this work from the combustion of benzoic acid (NIST SRM 39j), whose standard massic energy of combustion under certificate conditions was $\Delta_c u = -26\,434 \pm 3$ J·g^{-1} (see Supporting Information). Since the cresols are hygroscopic and prone to oxidation by air or oxygen, each sample under study was sealed in a polyethylene ampule of massic energy of combustion $\Delta_c u° = -46\,367.07 \pm 5.07$ J·g^{-1}, inside a glovebox, prior to the calorimetric experiments. The filled ampule was placed in a platinum crucible and weighed to ±10^{-5} g with a Mettler AT201 balance. The crucible with the sample was adjusted to the sample holder in the bomb head. The cotton thread fuse of empirical formula $CH_{1.887}O_{0.902}$ and $\Delta_c u° = -16\,565.9 \pm 8.6$ J·g^{-1} [42] was tied to the platinum ignition wire (Johnson Matthey; mass fraction 0.9995; diameter 0.05 mm), which was then connected between the two discharge electrodes. A volume of 1.0 cm^3 of distilled and deionized water from a Millipore system (conductivity, <0.1 μS·cm^{-1}) was added to the bomb body by means of a volumetric pipet. The stainless-steel bomb (Parr 1108) of 340 cm^3 internal volume was assembled and purged twice by successively charging it with oxygen at a pressure of 1.01 MPa and venting the overpressure. After purging, the bomb was charged with oxygen at a pressure of 3.04 MPa and a few minutes was allowed for equilibration before the inlet valve was closed. The bomb was placed in the calorimeter proper, inside the thermostatic bath. On average the calorimeter proper contained 3751.13 g of distilled water. The combustion of the sample was initiated by discharge of a 2990 μF capacitor from a potential of 40 V through the platinum wire.

The nitric acid formed in the calorimetric process from traces of atmospheric N_2 remaining inside the bomb after purging was determined by titration with aqueous sodium hydroxide (Merck titrisol, 0.01 mol·dm^{-3}), using methyl red as the indicator.

Calvet Drop Microcalorimetry. The enthalpies of sublimation of *o*- and *p*-cresols and the enthalpy of vaporization of *m*-cresol were measured by using the electrically calibrated Calvet drop sublimation microcalorimeter and the operating procedure previously reported.[43,44] The samples with masses in the ranges 6−14 mg (*o*-cresol), 7−19 mg (*m*-cresol), and 11−19 mg (*p*-cresol) were placed in small glass capillaries closed by Parafilm "M" tape and weighed with a precision of $\pm 10^{-6}$ g in a Mettler M5 microbalance. The capillaries were equilibrated inside a furnace placed above the entrance of the calorimetric cell for ca. 10 min and subsequently dropped into the calorimeter, under N_2 atmosphere, after removal of the Parafilm tape. The temperatures of the furnace and the calorimetric cell were both set to 298.15 K. After dropping, the sample and reference cells were simultaneously evacuated to 0.13 Pa and the measuring curve corresponding to the sublimation/vaporization of the sample was acquired. The enthalpy of sublimation/vaporization of the sample was subsequently derived from the area of the obtained curve and the calibration constant of the apparatus. No decomposition residues were found inside the calorimetric cell at the end of the experiments.

Computational Details. Density functional theory (DFT),[45] coupled cluster with single and double excitations (CCSD),[46,47] and complete basis set extrapolation (CBS-QB3)[48,49] procedures were applied to predict thermochemical properties for the systems of interest. In the case of the DFT methods full geometry optimizations and frequency predictions were carried out with the B3LYP,[50,51] B3P86,[52,53] and MPW1PW91[54,55] hybrid functionals, using the cc-pVDZ and cc-pVTZ basis sets.[56−58] The corresponding electronic energies at 0 K were converted to standard enthalpies at 298.15 K by using zero point energy and thermal energy corrections calculated at the same level of theory. The coupled cluster calculations of standard enthalpies at 298.15 K were made at the CCSD/cc-pVDZ//B3LYP/cc-pVTZ level of theory, using zero point energy and thermal energy corrections obtained by the B3LYP/cc-pVTZ method. All calculations were performed with the Gaussian 03 package.[59]

Results and Discussion

The 2005 IUPAC recommended standard atomic masses were used in the calculation of all molar quantities.[60]

Enthalpies of Formation and Vaporization/Sublimation of the Cresols. The standard specific internal energies and standard molar enthalpies of combustion of *o*-, *m*-, and *p*-cresols at 298.15 K, obtained in the combustion calorimetry experiments were $\Delta_c u°(o\text{-}CH_3C_6H_4OH,cr) = -34\,122.77 \pm 9.62$ J·g^{-1} and $\Delta_c H_m°(o\text{-}CH_3C_6H_4OH,cr) = -3692.7 \pm 2.9$ kJ·mol^{-1}, $\Delta_c u°(m\text{-}CH_3C_6H_4OH,l) = -34\,193.22 \pm 5.61$ J·g^{-1} and $\Delta_c H_m°(m\text{-}CH_3C_6H_4OH,l) = -3699.8 \pm 2.3$ kJ·mol^{-1}, and $\Delta_c u°(p\text{-}CH_3C_6H_4OH,cr) = -34\,141.64 \pm 11.44$ J·g^{-1} and $\Delta_c H_m°(p\text{-}CH_3C_6H_4OH,cr) = -3694.9 \pm 2.8$ kJ·mol^{-1}, respectively. The uncertainties quoted for $\Delta_c u°$ represent the standard deviation of the mean of five individual results (see Supporting Information), and those of $\Delta_c H_m°$ correspond to twice the overall standard deviation of the mean, including the contributions from the calibration with benzoic acid and from the combustion of the polyethylene ampules.[61,62] The above results refer to the reaction

$$C_7H_8O(cr,l) + 8.5O_2(g) = 7CO_2(g) + 4H_2O \qquad (1)$$

and lead to the corresponding standard molar enthalpies of formation listed in Table 1, by using $\Delta_f H_m°(CO_2,g) = -393.51 \pm 0.13$ kJ·mol^{-1} [63] and $\Delta_f H_m°(H_2O,l) = -285.830 \pm 0.040$ kJ·mol^{-1}.[63] Also included in Table 1 are the enthalpies of formation of the cresols in the solid or liquid state recalculated from the enthalpies of combustion previously reported in the literature. The values published by Stohmann,[11,12] Barker,[13] and Swarts[14] are only of historical value, and are not mentioned in major thermochemical compilations.[41,64,65] In these cases, for example, no reliable purity assessment was made, and no standard state corrections or uncertainties were considered in the calculation of $\Delta_c u°$ values from which the $\Delta_f H_m°$ data were derived. No standard state corrections or uncertainties were also taken into account in the work by Pushin,[15] Andon et al.,[16] and Bertholon.[18] The values reported by Cox[17] agree with those obtained in this work within the combined uncertainty intervals.

The enthalpies of sublimation or vaporization of the cresols obtained by Calvet drop microcalorimetry at 298.15 K are compared in Table 1 with the corresponding values from the literature. Andon et al.[16] derived $\Delta_{sub}H_m°(o\text{-}CH_3C_6H_4OH) = 76.0 \pm 0.8$ kJ·mol^{-1} based on vapor pressure against temperature data determined by ebulliometric and gas saturation methods. This value differs by 2.3 kJ·mol^{-1} from that proposed in this work (73.74 ± 0.46 kJ·mol^{-1}). The same authors obtained $\Delta_{vap}H_m°(m\text{-}CH_3C_6H_4OH) = 61.7 \pm 1.0$ kJ·mol^{-1}, which is 3.3 kJ·mol^{-1} lower than $\Delta_{vap}H_m°(m\text{-}CH_3C_6H_4OH) = 64.96 \pm 0.69$ kJ·mol^{-1} recommended in this work.

The reliability of other published $\Delta_{vap}H_m°(m\text{-}CH_3C_6H_4OH)$ data is difficult to assess since no uncertainties were indicated by the authors.[21−25] Note that the enthalpies of vaporization of *m*-cresol in Table 1 corresponding to the work of Nasir et al.,[23] Von Terres et al.,[24] and Goldblum et al.[25] were corrected from their reference temperatures, *T*, to 298.15 K by using

$$\Delta_{vap}H_m°(298.15\text{ K}) = \Delta_{vap}H_m°(T) + [C_{p,m}°(g) - C_{p,m}°(l)](298.15 - T) \quad (2)$$

where $C_{p,m}°(g)$ and $C_{p,m}°(l)$ are the molar heat capacities of the compound in the gaseous and liquid states at 298.15 K, respectively. The value $C_{p,m}°(g) = 128.6$ J·mol^{-1}·K^{-1} was calculated in this work by the B3LYP/cc-pVDZ method using frequencies scaled by 0.97,[66] and $C_{p,m}°(l) = 224.9$ J·mol^{-1}·K^{-1} was obtained from the literature.[16] The enthalpy of sublimation of *p*-cresol reported by Andon et al.[16] $\Delta_{sub}H_m°(p\text{-}CH_3C_6H_4OH) = 73.9 \pm 1.5$ kJ·mol^{-1} is in excellent agreement with $\Delta_{sub}H_m°(p\text{-}CH_3C_6H_4OH) = 73.13 \pm 0.56$ kJ·mol^{-1} obtained in this work.

The $\Delta_f H_m°$(cr/l) and $\Delta_{sub}H_m°/\Delta_{vap}H_m°$ data for the cresols recommended above lead to $\Delta_f H_m°(o\text{-}CH_3C_6H_4OH,g) = -130.5 \pm 2.7$ kJ·mol^{-1}, $\Delta_f H_m°(m\text{-}CH_3C_6H_4OH,g) = -131.6 \pm 2.2$ kJ·mol^{-1}, and $\Delta_f H_m°(p\text{-}CH_3C_6H_4OH,g) = -129.1 \pm 3.1$ kJ·mol^{-1}. These values in conjunction with $\Delta_f H_m°(C_6H_6,g) = 82.6 \pm 0.7$ kJ·mol^{-1},[65] $\Delta_f H_m°(C_6H_5CH_3,g) = 50.5 \pm 0.5$ kJ·mol^{-1},[65] and $\Delta_f H_m°(C_6H_5OH,g) = -96.4 \pm 0.9$ kJ·mol^{-1} [65] allow the

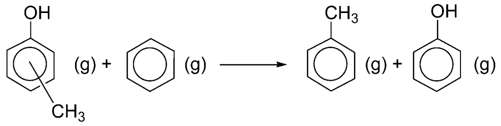
TABLE 1: Enthalpies of Formation and Vaporization/Sublimation of *o*-, *m*-, and *p*-Cresols at 298.15 K (Data in kJ·mol^{-1})

compound	$-\Delta_f H_m°$(cr,l)	$\Delta_{vap}H_m°/\Delta_{sub}H_m°$	$-\Delta_f H_m°$(g)
o-cresol, cr	204.2 ± 2.7^{a}	73.74 ± 0.46^{a}	130.5 ± 2.7^{a}
	200.5^{b,c}		
	201.3^{b-d}		
	204.3^{c,e}		
	204.3 ± 1.0^{f}	76.0 ± 0.8^{f,g,i}	128.3 ± 1.3
	204.6^{g}		
	204.6^{h}		
m-cresol, l	196.6 ± 2.1^{a}	64.96 ± 0.69^{a}	131.6 ± 2.2^{a}
	148.4^{c,j}		
	178.3^{c,e}		
	193.8^{c,k}		
	193.2 ± 1.0^{f}	61.7 ± 1.0^{f,g,i}	131.5 ± 1.0
	194.1^{g}		
	194.0^{h}		
	203.4^{b,c}		
	213.9^{b-d}		
		46.28^{l}	
		62.5^{m}	
		71.2^{n,o}	
		66.1^{o,p}	
		65.1^{o,q}	
p-cresol, cr	202.2 ± 3.0^{a}	73.13 ± 0.56^{a}	129.1 ± 3.1^{a}
	194.6^{c,e}		
	195.0^{b,c}		
	199.2 ± 1.0^{f,g}	73.9 ± 1.5^{f,g,i}	125.3 ± 1.8
	199.3^{h}		
	201.7^{b-d}		

[a] This work. [b] Reference13. [c] No Washburn corrections were taken into account. [d] References 11 and 12. [e] Reference 15. [f] Reference 17. [g] Reference 16. [h] Reference 18. [i] Reference 20. [j] Reference 14. [k] Reference 19. [l] Reference 21. [m] Reference 22. [n] Reference 23. [o] Corrected from the reference temperature of the experiments to 298.15 K (see text). [p] Reference 24. [q] Reference 25.

TABLE 2: Theoretical and Experimental Enthalpies of Reactions 3−5 at 298.15 K (Data in kJ·mol^{-1})

	B3LYP/cc-pVDZ	B3LYP/cc-pVTZ	B3P86/cc-pVDZ	B3P86cc-pVTZ	MPW1PW91/cc-Pvtz	CBS-QB3	CCSD/cc-pVDZ//B3LYP/cc-pVTZ	experiment
reaction 3								
o-cresol	2.1	1.0	2.1	1.0	0.2	3.7	3.2	2.0 ± 3.0
m-cresol	0.2	0.5	0.2	0.4	−0.4	0.5	0.7	3.1 ± 2.5
p-cresol	−2.0	−2.2	−2.0	−2.3	−3.1	−1. 3	−1.6	0.6 ± 3.3
reaction 4								
o-$CH_3C_6H_4O^•$	−8.8	−8.9	−9.4	−9.5	−3.5	−7. 4	−7.3	
m-$CH_3C_6H_4O^•$	−1.8	−1.9	−1.9	−2.0	−2.7	−2. 7	−1.6	
p-$CH_3C_6H_4O^•$	−7.9	−8.5	−8.1	−8.8	−9.2	−7. 7	−6.2	
reaction 5								
o-$CH_3C_6H_4O^•$	−10.9	−9.9	−11.5	−10. 5	−3.7	−11.1	−10.5	
m-$CH_3C_6H_4O^•$	−2.0	−2.3	−2.1	−2.3	−2.3	−3. 3	−2.3	
p-$CH_3C_6H_4O^•$	−5.9	−6.3	−6.1	−6.5	−6.1	−6. 3	−4.5	



(3)

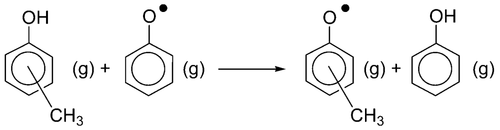
calculation of the enthalpy of the isodesmic and isogyric reaction 3. As shown in Table 2, the trend of the experimental $\Delta_r H_m°$(reaction 3) values (meta > ortho > para) is not perfectly reproduced by the predictions of the seven theoretical models used in this work (ortho > meta > para). The deviations between the computed and experimental results are, however, small particularly when the experimental uncertainties are taken into account. This supports the reliability of the computational methods and indicates a very good thermodynamic consistency between their estimates and the corresponding experimental values derived from standard enthalpy of formation data. The computed $\Delta_r H_m°$(reaction 3) values and the enthalpies of formation of benzene, toluene, and phenol indicated above also lead to the following enthalpies of formation of the gaseous cresols, where the uncertainties quoted refer to the contributions of the experimental data used in the calculation: $\Delta_f H_m°$(*o*-$CH_3C_6H_4OH$,g) = −130.6 ± 1.2 kJ·mol^{-1} (B3LYP/cc-pVDZ), −129.5 ± 1.2 kJ·mol^{-1} (B3LYP/cc-pVTZ), −130.6 ± 1.2 kJ·mol^{-1} (B3P86/cc-pVDZ), −129.5 ± 1.2 kJ·mol^{-1} (B3P86/cc-pVTZ), −128.7 ± 1.2 kJ·mol^{-1} (MPW1PW91/cc-pVTZ), −132.2 ± 1.2 kJ·mol^{-1} (CBS-QB3), −131.7 ± 1.2 kJ·mol^{-1} (CCSD/cc-pVDZ//B3LYP/cc-pVTZ); $\Delta_f H_m°$(*m*-$CH_3C_6H_4OH$,g) = −128.7 ± 1.2 kJ·mol^{-1} (B3LYP/cc-pVDZ), −129.0 ± 1.2 kJ·mol^{-1} (B3LYP/cc-pVTZ), −128.7 ± 1.2 kJ·mol^{-1} (B3P86/cc-pVDZ), −128.9 ± 1.2 kJ·mol^{-1} (B3P86/cc-pVTZ), −128.1 ± 1.2 kJ·mol^{-1} (MPW1PW91/cc-pVTZ), −129.0 ± 1.2 kJ·mol^{-1} (CBS-QB3), −129.2 ± 1.2 kJ·mol^{-1} (CCSD/cc-pVDZ//B3LYP/cc-pVTZ); $\Delta_f H_m°$(*p*-$CH_3C_6H_4OH$,g) = −126.5 ± 1.2 kJ·mol^{-1} (B3LYP/cc-pVDZ), −126.3 ± 1.2 kJ·mol^{-1} (B3LYP/cc-pVTZ), −126.5 ± 1.2 kJ·mol^{-1} (B3P86/cc-pVDZ), −126.2 ± 1.2 kJ·mol^{-1} (B3P86/cc-pVTZ), −125.4 ± 1.2 kJ·mol^{-1} (MPW1PW91/cc-pVTZ), −127.2 ± 1.2 kJ·mol^{-1} (CBS-QB3), −126.9 ± 1.2 kJ·mol^{-1} (CCSD/cc-pVDZ//B3LYP/cc-pVTZ). It is concluded that, with the exception of the MPW1PW91/cc-pVTZ prediction for *m*-cresol, all the obtained $\Delta_f H_m°$(g) values agree with the

TABLE 3: Enthalpies of Formation of the Methylphenoxyl Radicals Relative to the Enthalpy of Formation of the Phenoxyl Radical at 298.15 K (Data in kJ·mol^{-1})

	$\Delta_f H_m°(C_6H_5O^•,g) - \Delta_f H_m°(CH_3C_6H_4O^•,g)$/kJ·mol^{-1}		
method/reaction	o-$CH_3C_6H_4O^•$	m-$CH_3C_6H_4O^•$	p-$CH_3C_6H_4O^•$
B3LYP/cc-pVDZ			
reaction 4	42.9 ± 2.8	37.0 ± 2.4	40.6 ± 3.2
reaction 5	43.0 ± 0.9	34.1 ± 0.9	38.0 ± 0.9
B3LYP/cc-pVTZ			
reaction 4	43.0 ± 2.8	37.1 ± 2.4	41.2 ± 3.2
reaction 5	42.0 ± 0.9	34.4 ± 0.9	38.4 ± 0.9
B3P86P/cc-pVDZ			
reaction 4	43.5 ± 2.8	37.1 ± 2.4	40.8 ± 3.2
reaction 5	43.6 ± 0.9	34.2 ± 0.9	38.2 ± 0.9
B3P86P/cc-pVTZ			
reaction 4	43.6 ± 2.8	37.2 ± 2.4	41.5 ± 3.2
reaction 5	42.6 ± 0.9	34.4 ± 0.9	38.6 ± 0.9
MPW1PW91/cc-pVTZ			
reaction 4	37.6 ± 2.8	37.9 ±2.4	41.9 ± 3.2
reaction 5	35.8 ± 0.9	34.4 ± 0.9	38.2 ± 0.9
CBS-QB3			
reaction 4	41.5 ± 2.8	37.9 ± 2.4	40.4 ± 3.2
reaction 5	43.2 ± 0.9	35.4 ± 0.9	38.4 ± 0.9
CCSD/cc-pVDZ//B3LYP/cc-pVTZ			
reaction 4	41.4 ± 2.8	36.8 ± 2.4	38.9 ± 3.2
reaction 5	42.6 ± 0.9	34.4 ± 0.9	36.6 ± 0.9

corresponding experimental results in Table 1 within their combined uncertainty intervals.

Enthalpies of Formation of Methylphenoxyl Radicals and O−H Bond Dissociation Enthalpies in Cresols. The differences between the standard enthalpies of formation of the *o*-, *m*-, and *p*-methylphenoxyl radicals relative to the enthalpy of formation of the phenoxyl radical in the gaseous state, at 298.15 K, were estimated from the enthalpies of reactions 4 and 5 computed by the B3LYP/cc-pVDZ, B3LYP/cc-pVTZ, B3P86/cc-pVDZ, B3P86/cc-pVTZ, MPW1PW91/cc-pVTZ, CBS-QB3, and CCSD/cc-pVDZ//B3LYP/cc-pVTZ methods. The obtained $\Delta_r H_m°$ values are shown in Table 2. The averages of the $\Delta_r H_m°$ results predicted for reaction 4 by the different DFT models are −8.0 kJ·mol^{-1} (*o*-cresol), −2.1 kJ·mol^{-1} (*m*-cresol), and −8.5 kJ·mol^{-1} (*p*-cresol). The corresponding values for reaction 5 are −9.3 kJ·mol^{-1} (*o*-cresol), −2.2 kJ·mol^{-1} (*m*-cresol), and −6.2 kJ·mol^{-1} (*p*-cresol). In general, the differences between these averages and the individual $\Delta_r H_m°$ values computed by each DFT method are smaller than 2 kJ·mol^{-1}, the only exception being the MPW1PW91/cc-pVTZ predictions for *o*-cresol, which show deviations of 4.5 kJ·mol^{-1} in the case of reaction 4 and 5.6 kJ·mol^{-1} for reaction 5. No significant dependence on the selected basis set is noted. It is also apparent in Table 2 that the DFT results for the enthalpies of reactions 4 and 5 are in very good agreement with the corresponding CBS-QB3 and CCSD predictions.



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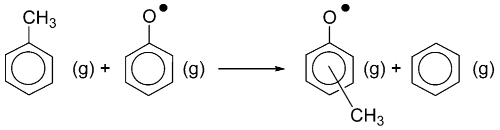

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By combining the data in Table 2 for reactions 4 and 5 with the enthalpies of formation of the cresols recommended in this work and $\Delta_f H_m°(C_6H_6,g) = 82.6 \pm 0.7$ kJ·mol^{-1},[65] $\Delta_f H_m°(C_6H_5CH_3,g) = 50.5 \pm 0.5$ kJ·mol^{-1},[65] and $\Delta_f H_m°(C_6H_5OH,g) = -96.4 \pm 0.9$ kJ·mol^{-1},[65] it is possible to derive the differences between the enthalpy of formation of the phenoxyl radical and the enthalpies of formation of the three methylphenoxyl radical isomers indicated in Table 3. These differences rather than the absolute values of $\Delta_f H_m°(CH_3C_6H_4O^•,g)$ were derived, since there is an ongoing debate in the literature about the "best" values for the enthalpy of formation of the phenoxyl radical and the O−H bond dissociation enthalpy in phenol, with recommended data spanning a range of ca. 16 kJ·mol^{-1}.[4,38,67,68] The overall uncertainties assigned to the values in Table 3 refer to the contributions of the uncertainties of the experimental data used in the calculation. In general, the $\Delta_f H_m°(C_6H_5O^•,g) - \Delta_f H_m°(CH_3C_6H_4O^•,g)$ values predicted from reactions 4 and 5 by all models are in good agreement within their combined uncertainty intervals. The mean of the results obtained for each cresol by the higher level theoretical methods (CBS-QB3 and CCSD/cc-pVDZ//B3LYP/cc-pVTZ), with the larger uncertainty of the corresponding individual values, were selected in this work as $\Delta_f H_m°(C_6H_5O^•,g) - \Delta_f H_m°(o\text{-}CH_3C_6H_4O^•,g) = 42.2 \pm 2.8$ kJ·mol^{-1}, $\Delta_f H_m°(C_6H_5O^•,g) - \Delta_f H_m°(m\text{-}CH_3C_6H_4O^•,g) = 36.1 \pm 2.4$ kJ·mol^{-1}, and $\Delta_f H_m°(C_6H_5O^•,g) - \Delta_f H_m°(p\text{-}CH_3C_6H_4O^•,g) = 38.6 \pm 3.2$ kJ·mol^{-1}. These differences, together with the enthalpies of formation of the cresols recommended in this work and $\Delta_f H_m°(C_6H_5OH,g) = -96.4 \pm 0.9$ kJ·mol^{-1},[65] yield the following $DH°(C_6H_5O{-}H) - DH°(CH_3C_6H_4O{-}H)$ values at 298.15 K: $DH°(C_6H_5O{-}H) - DH°(o\text{-}CH_3C_6H_4O{-}H) = 8.1 \pm 4.0$ kJ·mol^{-1}, $DH°(C_6H_5O{-}H) - DH°(m\text{-}CH_3C_6H_4O{-}H) = 0.9 \pm 3.4$ kJ·mol^{-1}, and $DH°(C_6H_5O{-}H) - DH°(p\text{-}CH_3C_6H_4O{-}H) = 5.9 \pm 4.5$ kJ·mol^{-1}. These values indicate that $DH°(C_6H_5O{-}H) > DH°(CH_3C_6H_4O{-}H)$ for the three cresol isomers, in keeping with the general observation that electron-donating substituents weaken the O−H bond in monosubstituted phenols, relative to phenol.[4] The differences $DH°(C_6H_5O{-}H) - DH°(CH_3C_6H_4O{-}H)$ obtained in this work are compared in Table 4 with corresponding results from experimental and theoretical methods reported in the literature.[4,26−38]

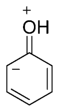
As noted in the Introduction, much better agreement is observed when the $DH°(C_6H_5O{-}H) - DH°(CH_3C_6H_4O{-}H)$ differences proposed by different authors, rather than the absolute $DH°(CH_3C_6H_4O{-}H)$ values, are considered. This

TABLE 4: O−H Bond Dissociation Enthalpies in *o*-, *m*-, and *p*-Cresols, at 298.15 K, Relative to Phenol (Data in $kJ\cdot mol^{-1}$)

$DH°(C_6H_5O-H) - DH°(MeC_6H_4O-H)$		
o-cresol	*m*-cresol	*p*-cresol
8.1 ± 4.0[a]	0.9 ± 3.4[a]	5.9 ± 4.5[a]
6.9[b]	1.9[b]	7.2[h]
6.7[c]	1.7[e]	8.8[i]
9 ± 4[d]	6.7[c]	18.7[j]
	5.0[f]	4.8[b]
	4.9[g]	7.1[e]
	3 ± 4[d]	8.8[k]
		8.0[c]
		7.5[l]
		4.8[m]
		8.4[n]
		3.0[o]
		−1.0[p]
		−3.0[q]
		6.2[r]
		10.8[g]
		8 ± 4[d]

[a] This work. [b] Reference 28; based on a correlation of gas phase $DH°(O-H)$ with pK_a and oxidation potential data obtained in solution. [c] Reference 34; AM1/AM1//B3LYP/6-31G(,p′), most stable conformation. [d] Recommended in ref 4. [e] Reference 29; based on a correlation of gas phase $DH°(O-H)$ with pK_a and oxidation potential data obtained in solution. [f] Reference 38; experimental gas phase acidity data combined with electron affinity calculated by the CBS-QB3 method. [g] Reference 4; $DH°(C_6H_5O-H) - DH°(CH_3C_6H_4O-H)$ derived from a correlation with Hammett's σ^+ parameter. [h] Reference 32; kinetic studies in solution. [i] Reference 26; $DH°(O-H)$ derived from a thermodynamic cycle involving pK_a and oxidation potential data obtained in solution. [j] Reference 27; based on a correlation of gas phase $DH°(O-H)$ with pK_a and oxidation potential data obtained in solution. [k] Reference 33; based on equilibrium studies in solution by EPR spectroscopy. [l] Reference 35; B3LYP/6-31G(d,p). [m] Reference 30; based on a correlation of gas phase $DH°(O-H)$ with pK_a and oxidation potential data obtained in solution. [n] Reference 36; HSAB+B3LYP/6-31+G(d). [o] Reference 37; UB3LYP/6-311+G(2d,2p). [p] Reference 37; AM1. [q] Reference 37; PM3. [r] Reference 31; $DH°(C_6H_5O-H) - DH°(CH_3C_6H_4O-H)$ derived from a correlation with pK_a and reduction potential data obtained in solution.

situation is unlikely to improve until a general consensus is reached about the value of $DH°(C_6H_5O-H)$.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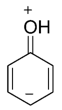
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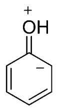
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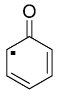
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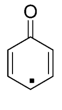
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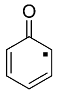
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The relative stabilities of the cresols and of the corresponding methylphenoxyl radicals in the gas phase, as measured by the differences in their Gibbs energies of formation at 298.15 K, can be analyzed by using the standard enthalpies of formation (or their differences relative to phenol in the case of the radicals) recommended in this work and the following entropy values: $S_m°(o\text{-}CH_3C_6H_4OH,g) = 352.70\ J\cdot K^{-1}\cdot mol^{-1}$, $S_m°(m\text{-}CH_3C_6H_4OH,g) = 356.15\ J\cdot K^{-1}\cdot mol^{-1}$, $S_m°(p\text{-}CH_3C_6H_4OH,g) = 350.86\ J\cdot K^{-1}\cdot mol^{-1}$, $S_m°(o\text{-}CH_3C_6H_4O^\bullet,g) = 352.41\ J\cdot K^{-1}\cdot mol^{-1}$, $S_m°(m\text{-}CH_3C_6H_4O^\bullet,g) = 354.00\ J\cdot K^{-1}\cdot mol^{-1}$, and $S_m°(p\text{-}CH_3C_6H_4O^\bullet,g) = 354.28\ J\cdot K^{-1}\cdot mol^{-1}$. The entropies of the cresols at 298.15 K were taken from the literature,[69] and those of the corresponding radicals were obtained by statistical thermodynamics calculations[70] using structural data and vibration frequencies predicted by the B3LYP/cc-pVTZ method (see Supporting Information). The frequencies were scaled by 0.965.[66] The internal rotation of the methyl group was accepted as free in the case of the meta and para isomers, and hindered in the case of the ortho isomer. The contribution of the hindered rotation for the entropy of the *o*-methylphenoxyl radical was taken from the tables of Pitzer and Gwin,[71] and based on a potential barrier height $V = 3.6\ kJ\cdot mol^{-1}$ calculated at the B3LYP/cc-pVTZ level assuming a rigid-rotor model. The electronic contribution was taken as $S_m°_{el} = R \ln 2$ for the three radicals. The obtained differences in $\Delta_f G_m°$ relative to the ortho isomers ($\Delta\Delta_f G_m°$) were $\Delta\Delta_f G_m°(m\text{-}CH_3C_6H_4OH,g) = -2.1\ kJ\cdot mol^{-1}$, $\Delta\Delta_f G_m°(p\text{-}CH_3C_6H_4OH,g) = 1.9\ kJ\cdot mol^{-1}$, $\Delta\Delta_f G_m°(m\text{-}CH_3C_6H_4O^\bullet,g) = 5.6\ kJ\cdot mol^{-1}$, and $\Delta\Delta_f G_m°(p\text{-}CH_3C_6H_4O^\bullet,g) = 3.0\ kJ\cdot mol^{-1}$. These results are represented in Figure 1 along with the corresponding differences in enthalpy of formation. Figure 1 suggests that the stability of the cresols varies according to *p*-cresol < *o*-cresol < *m*-cresol, and that of the radicals follows the trend *m*-methylphenoxyl < *p*-methylphenoxyl < *o*-methylphenoxyl. It also indicates that these tendencies are enthalpically controlled. Qualitatively, the inversion in the order of stability of the meta isomer relative to the ortho and para counterparts on going from the cresol series to the corresponding methylphenoxyl radicals is in agreement with the prediction of simple resonance theory. The electron-donating methyl group in *m*-cresol is not expected to influence the contributions of the quinonoid resonance structures **4**−**6**. On the other hand, ortho and para substitutions oppose the presence of the negative charge in those structures, thus destabilizing *o*-cresol and

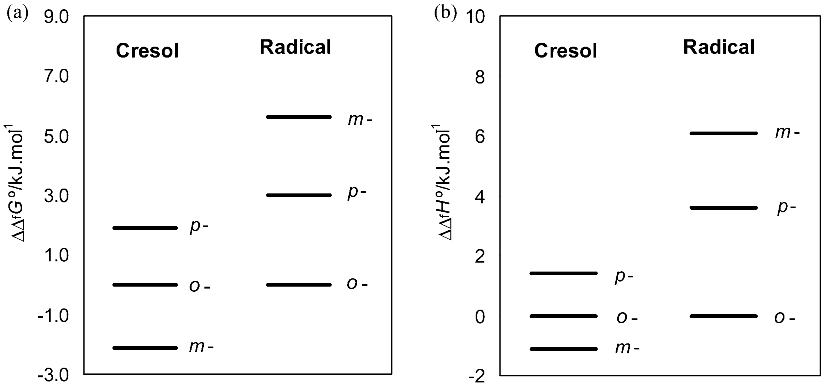

Figure 1. Relative stabilities of the cresols and of the corresponding methylphenoxyl radicals in terms of (a) differences in Gibbs energy of formation, $\Delta\Delta_f G_m°$, and (b) differences in enthalpy of formation, $\Delta\Delta_f H_m°$.

p-cresol relative to *m*-cresol. In the radicals resonance delocalization of the odd electron through structures **7**−**9** is favored by the presence of the electron-donating methyl group in the ortho and para positions, hence stabilizing the *o*- and *p*-methylphenoxyl radicals relative to the *m*-methylphenoxyl radical.

Acknowledgment. This work was supported by Fundação para a Ciência e a Tecnologia (FCT), Portugal. A Ph.D. grant from FCT is gratefully acknowledged by C.E.S.B. We also thank Prof. J. A. Martinho Simões (FCUL), Dr. R. M. Borges dos Santos (Universidade do Algarve), and Prof. K. U. Ingold (IMS-NRC, Canada) for helpful suggestions, and Dr. J. Branco (ITN) for the GC analysis.

Supporting Information Available: Details of the combustion calorimetric experiments including Tables S1−S3 with the results of all individual runs carried out on the cresols and Table S4 with the auxiliary data used for the standard state correction. Table S5 with the electronic energies, thermal corrections, zero point energies, and enthalpies at 298.15 K for all species studied by the B3LYP/cc-pVDZ, B3LYP/cc-pVTZ, B3P86/cc-pVDZ, B3P86/cc-pVTZ, and MPW1PW91/cc-pVTZ, CBS-QB3, and CCSD/cc-pVDZ//B3LYP/cc-pVTZ methods. Tables S6−S9 with the details of the statistical thermodynamics calculations of the entropies of the methylphenoxyl radicals. This material is available free of charge via the Internet at http://pubs.acs.org.

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