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Thermochemical and Theoretical Study of *tert*-Butyl and Di-*tert*-butylphenol Isomers

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The standard ($p^o = 0.1$MPa) molar enthalpies of formation for 2-, 3-, and 4-*tert*-butylphenol and 2,4- and 2,6-di-*tert*-butylphenol in the gaseous phase were derived from the standard molar enthalpies of combustion, in oxygen, at 298.15 K, measured by static bomb combustion calorimetry and the standard molar enthalpies of evaporation at 298.15 K, measured by Calvet microcalorimetry: 2-*tert*-butylphenol, −184.7 ± 2.6 kJ mol^{-1}; 3-*tert*-butylphenol, −198.0 ± 2.1 kJ mol^{-1}; 4-*tert*-butylphenol, −187.3 ± 3.3 kJ mol^{-1}; 2,4-di-*tert*-butylphenol −283.3 ± 3.8 kJ mol^{-1}; 2,6-di-*tert*-butylphenol −272.0 ± 4.0 kJ mol^{-1}. The most stable geometries of all mono- and disubstituted phenols as well as those of the corresponding radicals were obtained, respectively, by ab initio restricted Hartree−Fock (RHF) and restricted Hartree−Fock open shell (ROHF) methods with the 6-31G* basis set. The resulting geometries were then used to obtain estimates of the effect of the *tert*-butyl substituent on the O−H bond dissociation energy and on the formation enthalpies of all substituted phenols.

Introduction

The determination of the O−H bond dissociation enthalpies D_h(O−H) of phenolic molecules is of considerable practical interest since this class of chemical compounds includes most of the synthetic and naturally occurring antioxidants that exert their action via an initial hydrogen-transfer reaction whose rate constant depends on the strength of the O−H bond. There are many reports in the literature[1] of studies of the properties of the O−H bond, both in solution and in the gaseous state, using a diversity of modern experimental and computational methods. One of the main goals of these studies is the understanding of the stability of the phenolic bond and how this stability is affected by the number, nature, and position of the substituents in the aromatic ring.

In the present work, we report the standard molar enthalpies of formation in the gaseous state of the three isomers of *tert*-butylphenol and of 2,4- and 2,6-di-*tert*-butylphenol, obtained from measurements of combustion energies using a static bomb calorimeter and of the values for the enthalpies of sublimation or vaporization of the compounds measured by microcalorimetry. Ab initio calculations were performed in order to obtain the most stable geometries for these molecules and for all the other di-*tert*-butyl isomers, as well as for the corresponding radicals. The good agreement between the relative stabilities of the phenols studied both experimentally and theoretically allowed us to go further in the theoretical interpretation of the influence of the substituents on the energy of dissociation of the O−H bond, in the case of *tert*-butyl substitution.

Experimental Section

Materials. The phenols were obtained commercially from Aldrich Chemical Co., and they were purified by repeated vacuum distillation or sublimation until the combustion results were consistent and the carbon dioxide recovery ratios were satisfactory. The average ratios, together with the standard deviation of the mean, of the mass of carbon dioxide recovered to that calculated from the mass of sample were as follows: 2-*t*-BuPhOH, 0.9991 ± 0.0001; 3-*t*-BuPhOH, 0.9995 ± 0.0002; 4-*t*-BuPhOH, 0.9996 ± 0.0002; 2,4-*t*-Bu_2PhOH, 0.9993 ± 0.0004; 2,6-*t*-Bu_2PhOH, 0.9990 ± 0.0001. The densities of the samples were as follows: 2-*t*-BuPhOH, $\rho = 0.978$ g mL^{-1};[2] 4-*t*-BuPhOH, $\rho = 0.908$ g mL^{-1};[2] for the 3-*t*-BuPhOH we adopted the value used for the 4-*t*-BuPhOH ; for the di-*tert*-butylphenols the value for 2,4,6-tri-*tert*-butylphenol, $\rho = 0.864$ g mL^{-1},[2] was assumed. For all the compounds C and H microanalysis were used as an additional test of purity.

Combustion Calorimetry. The combustion experiments were performed with a static bomb calorimeter; apparatus and technique have been described.[3,4] Benzoic acid (Bureau of Analyzed Samples, Thermochemical Standard, BCS-CRM-190p) was used for calibration of the bomb. Its massic energy of combustion is $\Delta_c u = -26432.3 \pm 3.8$ J g^{-1}, under certificate conditions. The calibration results were corrected to give the energy equivalent ϵ_{cal} corresponding to the average mass of water added to the calorimeter: 3119.6 g. The uncertainties quoted are the standard deviations of the mean (see row ϵ_{cal} in Table 1). For all experiments, ignition was made at 298.150 ± 0.001 K. Combustion experiments were made in oxygen at $p = 3.04$ MPa, with 1.00 mL of water added to the bomb. The electrical energy for ignition ΔU(ign) was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire. For the cotton-thread fuse, empirical formula $CH_{1.686}O_{0.843}$, $\Delta_c u^o = -16250$ J g^{-1}.[5] This value has been checked in our laboratory. The corrections for nitric acid formation $\Delta U(HNO_3)$ were based on

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[1] Borges dos Santos, R.; Martinho Simões, J. A. *J. Phys. Chem. Ref. Data* **1998**, *27*, 708.

[2] *Handbook of Chemistry and Physics*, 70th ed.; Weast, R. C., Ed.; CRC Press Inc.: Cleveland, OH, 1989−1990.

[3] Ribeiro da Silva, M. A. V.; Ribeiro da Silva, M. D. M. C.; Pilcher, G. *Rev. Port. Quim.* **1984**, *26*, 163.

[4] Ribeiro da Silva, M. A. V.; Ribeiro da Silva, M. D. M. C.; Pilcher, G. *J. Chem. Thermodyn.* **1984**, *16*, 1149.

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Table 1. Typical Combustion Experiments at 298.15 K

	2-*t*-BuPhOH	3-*t*-BuPhOH	4-*t*-BuPhOH	2,4-*t*-Bu_2PhOH	2,6-*t*-Bu_2PhOH
m (CO_2, total)/g	2.081 92	1.970 74	1.872 11	2.000 34	2.080 62
m (compd)/g	0.656 85	0.670 59	0.637 03	0.667 73	0.694 38
m'(fuse)/g	0.003 70	0.003 78	0.003 60	0.003 92	0.004 36
m''(Melinex)/g	0.066 17				
ΔT_{ad}/K	1.647 74	1.576 74	1.499 45	1.673 36	1.745 28
ϵ_{cal}/(J K^{-1})	16 015.9 ± 0.7	16 006.4 ± 1.4	16 015.9 ± 0.7	16 015.9 ± 0.7	16 015.9 ± 0.7
ϵ_f/(J K^{-1})	16.79	16.72	16.58	16.93	17.04
$\Delta m(H_2O)$/g	0.0	0.1	0.0	0.0	0.0
$-\Delta U$(IBP)/J	26 417.70	25 264.95	24 039.90	26 828.70	27 981.97
$-\Delta U$(Melinex)/J	1515.52				
$-\Delta U$(fuse)/J	60.09	61.39	58.46	63.66	70.81
$-\Delta U(HNO_3)$/J	2.42	1.41	2.24	7.88	7.94
$-\Delta U$(carbon)/J	0.00	0.00	0.00	0.00	0.00
$-\Delta U$(ign)/J	0.57	0.57	0.47	0.40	0.46
$-\Delta U_\Sigma$/J	12.67	11.47	10.81	10.81	11.33
$-\Delta_c u^o$(compd)/(J g^{-1})	37 796.19	37 564.10	37 624.48	40 055.04	40 167.39

−59.7 kJ mol^{-1},[6] for the molar energy of formation of 0.1 mol L^{-1} HNO_3(aq) from N_2, O_2, and H_2O(l). The amount of substance m (compd) used in each experiment was determined from the total mass of carbon dioxide m (CO_2, total) produced after allowance for that formed from the cotton thread fuse and Melinex. Sealed Melinex bags were used in combustion of the liquid 2-*t*-BuPh, using the technique described by Skinner and Snelson,[7] who determined the specific energy of combustion of dry Melinex as $\Delta_c u^o = -22902 \pm 5$ J g^{-1}. That value was confirmed in our laboratory. The mass of Melinex used in each experiment was corrected for the mass fraction of water (0.0032).[7] An estimated pressure coefficient of specific energy: $(\partial u/\partial p)_T = -$ 0.2 J g^{-1} MPa^{-1} at 298.15 K, a typical value for most organic compounds, was assumed. For each compound, the massic energy of combustion, $\Delta_c u^o$, was calculated by the procedure given by Hubbard et al.[8] The molar masses used for the elements were those recommended by the IUPAC comission.[9]

Enthalpies of Sublimation and Vaporization. The enthalpies of sublimation and of vaporization (2-*tert*-butylphenol) were measured by using the "*vacuum sublimation*" drop microcalorimetric method,[10,11] which, in the case of vaporization, was previously tested in the Porto laboratory. Samples, about 3−5 mg of each solid compound and of 6−10 mg of the liquid 2-*tert*-butylphenol, contained in thin glass capillary tubes sealed at one end, were dropped, at room temperature, into the hot reaction vessel, in a high-temperature Calvet microcalorimeter held at a convenient temperature T and then removed from the hot zone by *vacuum* evaporation. The observed enthalpies of evaporation were corrected to 298.15 K by using the value of $\Delta_{298.15K}^{T} H^o{}_m$(g) estimated by a group method with values from Stull et al.[12] The microcalorimeter was calibrated in situ for these measurements by using the reported enthalpies of sublimation of naphthalene[12] and of vaporization of decane.[13]

Table 2. Values of $-\Delta_c u°$/(J g^{-1}) at 298.15 K

2-*t*-Bu-PhOH	3-*t*-Bu-PhOH	4-*t*-Bu-PhOH	2,4-*t*-Bu_2–PhOH	2,6-*t*-Bu_2–PhOH
37 787.06	37 547.23	37 634.75	40 047.33	40 180.19
37 769.62	37 551.08	37 640.72	40 049.44	40 140.64
37 784.21	37 564.10	37 642.32	40 059.26	40 157.48
37 792.00	37 549.83	37 624.48	40 064.18	40 189.94
37 796.19	37 550.54	37 611.46	40 066.89	40 158.53
37 776.39	37 560.27	37 615.62	40 056.42	40 195.09
	37 564.55	37 609.36	40 052.57	40 169.32
		37 610.88	40 055.04	40 143.93
				40 160.92
				40 167.39
		$-\langle\Delta_c u°\rangle$ (J g^{-1})		
37 784.2 ± 4.0	37 555.4 ± 2.8	37 623.7 ± 4.9	40 056.4; ± 2.4	40 166.3 ± 5.7

Table 3. Derived Standard ($p° = 0.1$ MPa) Molar Values (kJ mol^{-1}) at 298.15 K

	$-\Delta_c U^o_m$ (cr, l)	$-\Delta_c H^o_m$ (cr, l)	$-\Delta_f H^o_m$ (cr, l)
2-*t*-BuPhOH	5675.9 ± 2.0	5683.3 ± 2.0	252.6 ± 2.4
3-*t*-BuPhOH	5641.6 ± 1.5	5649.0 ± 1.5	286.9 ± 2.0
4-*t*-BuPhOH	5651.8 ± 1.7	5659.2 ± 1.7	276.7 ± 2.2
2,4-*t*-Bu_2PhOH	8264.7 ± 1.7	8277.1 ± 1.7	376.2 ± 2.5
2,6-*t*-Bu_2PhOH	8287.4 ± 2.7	8299.8 ± 2.7	353.5 ± 3.3

Experimental Results. Results for a typical combustion experiment of each compound are given in Table 1, where $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from 3119.6 g, and ΔU_Σ is the correction to the standard state. The remaining quantities are as previously described.[8] As samples were ignited at 298.15 K,

$$\Delta U(\mathrm{IBP}) = -[\epsilon_{\mathrm{cal}} + \Delta m(\mathrm{H_2O}) \cdot c_p(\mathrm{H_2O,l}) + \epsilon_f]\Delta T_{\mathrm{ad}} + \Delta U_{\mathrm{ign}}$$

where ΔU(IBP) is the energy associated to the isothermal bomb process, ϵ_f is the energy of the bomb contents after ignition, and ΔT_{ad} is the adiabatic temperature raise. The individual results of all combustion experiments, together with the mean value and its standard deviation, are given for each compound in Table 2. Table 3 lists the derived standard molar energies and enthalpies of combustion, $\Delta_c U^o{}_m$(cr,l) and $\Delta_c H^o{}_m$(cr,l), and the standard molar enthalpies of formation for the compounds in condensed phase $\Delta_f H^o{}_m$(cr,l) at 298.15 K. In accordance with normal thermochemical practice, the uncertainties assigned to the standard molar enthalpies of combustion are, in each case, twice the overall standard deviation of the mean and include the uncertainties in calibration[14] and in the values of auxiliary quantities. To derive $\Delta_f H^o{}_m$(cr,l) from $\Delta_c H^o{}_m$(cr,l), the standard molar enthalpies of formation of H_2O(l) and CO_2(g), at 298.15 K, − 285.830 ± 0.042 kJ mol^{-1} [15] and −393.51 ± 0.13 kJ mol^{-1},[15] respectively, were used.

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(5) Coops, J.; Jessup, R. S.; Van Nes, K. *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol. 1, Chapter 3.

(6) The NBS Tables of Chemical Thermodynamic Properties. *J. Phys. Chem. Ref. Data* **1982**.

(7) Skinner, H. A.; Snelson, A. *Trans. Faraday Soc.* **1960**, *56*, 1776.

(8) Hubbard, W. N.; Scott, D. W.; Waddington, G. *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol. 1, Chapter 5.

(9) I. U. P. A. C. *J. Phys. Chem. Ref. Data* **1997**, *26*, 1239.

(10) Adedeji, F. A.; Brown, D. L. S.; Connor, J. A.; Leung, M.; Paz-Andrade, M. I.; Skinner, H. A. *J. Organomet. Chem.* **1975**, *97*, 221.

(11) Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Amaral, L. M. P. F. *J. Chem. Thermodyn.* **1995**, *27*, 565.

(12) Stull, D. R.; Westrum, E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

(13) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds;* TRC Data Series: College Station, TX, 1994; Vol. I.

(14) Rossini, F. D. *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol. 1, Chapter 14, pp 297−320.

(15) *J. Chem. Thermodyn.* **1978**, *10*, 903.

Table 4. Microcalorimetric Standard ($p^o = 0.1$ MPa) Molar Enthalpies of Vaporization and Sublimation ($\mathrm{kJ \cdot mol^{-1}}$) at 298.15 K

	no. of expts	T/K	$\Delta_{\mathrm{cr,l}}^{\mathrm{g},T} H_m^{\mathrm{o}}$	$\Delta_{298.15\mathrm{K}}^{T} H_m^{\mathrm{o}}(\mathrm{g})$	$\Delta_{\mathrm{cr,l}}^{\mathrm{g}} H_m^{\mathrm{o}}$
2-*t*-BuPhOH (l)	5	366	82.9 ± 1.0	15.0	67.9 ± 1.0
3-*t*-BuPhOH (cr)	7	367	103.8 ± 0.5	14.9	88.9 ± 0.5
4-*t*-BuPhOH (cr)	6	380	107.1 ± 2.5	17.7	89.4 ± 2.5
2,4-*t*-$\mathrm{Bu_2}$PhOH (cr)	5	372	116.4 ± 2.8	23.5	92.9 ± 2.8
2,6-*t*-$\mathrm{Bu_2}$PhOH (cr)	7	373	105.7 ± 2.3	24.2	81.5 ± 2.3

Table 5. Derived Standard ($p^o = 0.1$ MPa) Molar Values ($\mathrm{kJ \cdot mol^{-1}}$) at 298.15 K

	$-\Delta_{\mathrm{f}} H_m^{\mathrm{o}}(\mathrm{cr,l})$	$\Delta_{\mathrm{cr,l}}^{\mathrm{g}} H_m^{\mathrm{o}}$	$-\Delta_{\mathrm{f}} H_m^{\mathrm{o}}(\mathrm{g})$
2-*t*-BuPhOH (l)	252.6 ± 2.4	67.9 ± 1.0	184.7 ± 2.6
3-*t*-BuPhOH (cr)	286.9 ± 2.0	88.9 ± 0.5	198.0 ± 2.1
4-*t*-BuPhOH (cr)	276.7 ± 2.2	89.4 ± 2.5	187.3 ± 3.3
2,4-*t*-$\mathrm{Bu_2}$PhOH (cr)	376.2 ± 2.5	92.9 ± 2.8	283.3 ± 3.8
2,6-*t*-$\mathrm{Bu_2}$PhOH (cr)	353.5 ± 3.3	81.5 ± 2.3	272.0 ± 4.0

Measurements of the enthalpies of sublimation and of vaporization $\Delta_{\mathrm{cr,l}}^{\mathrm{g}} H_m{}^{\mathrm{o}}$ are given in Table 4 with uncertainties of twice the standard deviation of the mean. The derived enthalpies of formation, in both the condensed and gaseous phases, for all the compounds are summarized in Table 5.

Ab Initio Calculations

The most stable geometries of phenol and of all possible mono- and disubstituted *tert*-butylphenol isomers, as well as of their corresponding radicals, have been obtained through full geometry optimization using single-determinant restricted Hartree–Fock (RHF) and restricted open-shell Hartree–Fock (ROHF) theories, with the 3-21G [16] and 6-31G*[17] Pople's split valence basis sets. The resulting optimum geometries were further characterized as true minima through construction and diagonalization of the 3-21G Hessian matrixes, this procedure providing also the harmonic vibrational frequencies and thermal corrections, which are needed to estimate energies at any temperature different from 0 K. In the case of the 2,4- and 2,6-neutral isomers, the conformations predicted using the 6-31G* are qualitatively different from those obtained with the 3-21G basis set, this fact forcing us to estimate the vibrational frequencies and thermal corrections from the 6-31G* Hessians. To account, at least partially, for the correlation error, we also performed single-point energy calculations using density functional theory (DFT) within the nonlocal spin density approximation (NLSDA) for all species and Møller–Plesset perturbation theory calculations truncated at the second-order of the perturbational expansion (MP2), for all closed-shell species. The size of the required basis sets prevented the MP2 calculations to be extended to the radicals. For the DFT calculations, the local component of the functional, for the exchange-correlation energy density and the corresponding potentials, were modeled according to the Vosko–Wilk–Nursair[18] local functional while the nonlocal corrections are represented by nonlocal functionals of Becke[19] (for exchange) and Perdew[20] (for correlation). We used also a double-ζ quality basis set that has been properly optimized for this type of calculation.[21] In this basis set, which is roughly equivalent to Pople's 6-31G* one, the H atom basis set has a (41) contraction pattern whereas first-row atoms are represented by a (721/51/1*) basis (using Huzinaga's notation).[22] In addition, DFT calculations require auxiliary sets of functions to fit the charge density and the exchange-correlation potential. For hydrogen atoms, the two sets of functions consisted of four uncontracted *s*-type Gaussians, while for the first-row atoms they consisted of four uncontracted *s*-type Gaussians and three uncontracted Gaussians. The MP2 calculation used the basis set 6-31G*. All ab initio calculations were performed using the quantum mechanical program GAMESS,[23] while the density functional results were obtained using an academic version of deMon program.[24]

Results and Discussion

All substituted phenol and corresponding radicals show planar phenolic aromatic rings within the 6-31G* level, the only exception being the 2,3-di-*tert*-butylphenol and its radical. In these cases, the phenolic ring showed considerable deviation from planarity as evidenced by a large dihedral angle of ca. 17° within the ring. This deviation can be attributed to the large steric hindrance that occurs between the two bulky substituent groups attached at positions close to the oxygen atom and must reflect on the relative stabilities of the 2,3-disubstituted species since the electron delocalization though the aromatic ring is then severely restricted. The same repulsion effect can also be observed in the orientation of the two C-*t*-Bu bonds in the 2,3-disubstituted species toward different sides of the ring and in the deviations of the directions of those bonds from the directions bissecting the C–C–C ring angles at the central atoms at which the substituents are attached; this last effect is also apparent in the 3,4-disubstituted species, and it has the same magnitude of ca. 8°.

The O–H bonds of the substituted phenol molecules are found to be coplanar with the phenolic ring, a fact well-known for the nonsubstituted molecule, which is an indication that delocalization of the π-lone-pair of the oxygen atoms is more effective than the delocalization of the σ-lone-pair. On the other hand, all phenoxyl radicals are found to have their unpaired electron occupying a π-oxygen orbital; i.e., they are π radicals.

The predicted C–O bond lengths show a remarkable constancy within each class of molecules: 1.35–1.36 Å (substituted phenol); 1.32–1.35 Å (substituted phenoxyl radical). This shortening of the C–O bond can probably be correlated with a progressive increase of double-bond character of the C–O bond as we consider the phenol molecules and the radicals.

The resulting energies of all species are collected in Table 6 and allowed us to estimate the relative stabilities

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[16] Binkley, J. S.; Pople, J. A.; Hehre, J. W. *J. Am. Chem. Soc.* **1980**, *102*, 939. Gordon, J. S. Binkley, M. S., Pople, J. A.; Pietro, W. J.; Hehre, J. W. *J. Am. Chem. Soc.* **1982**, *104*, 2797.

[17] Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *66*, 217. Francl, M. M.; Pietro, W. J.; Hehre, J. W.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

[18] Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

[19] Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098.

[20] J. P. Perdew, A. D. *Phys. Rev.* **1986**, *B33*, 6622.

[21] Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560.

[22] *Gaussian Basis Sets for Molecular Calculations*; Huzinaga, S., Ed.; Elsevier: New York, 1984.

[23] Dupuis, M.; Spangler, D.; Wendoloski, J. J. *NRCC Software Catalog*, Program QG10, 1980. Schimdt, M. W.; Boatz, J. A.; Baldridge, K. K.; Koseki, S.; Gordon, M. S.; Elbert, S. T.; Lam, B. *QCPE Bull.* **1987**, *7*, 115.

[24] St-Amant, A.; Salahub, D. R. *Chem. Phys. Lett.* **1990**, *169*, 169. St-Amant, A. Ph.D. Thesis, Université de Montréal, 1992.

Table 6. Calculated Energies for All Species (in Atomic Units)

	phenol		phenoxyl radical
compd	MP2	DFT/NLSDA	DFT/NLSDA
PhOH	−306.488 703 7	−307.555 163 9	−306.907 498 0
2-*t*-BuPhOH	−463.161 375 4	−464.846 716 6	−464.207 193 5
3-*t*-BuPhOH	−463.161 457 5	−464.849 727 6	−464.206 112 3
4-*t*-BuPhOH	−463.161 149 0	−464.849 169 2	−464.207 424 0
2,3-*t*-Bu$_2$PhOH	−619.788 046 2	−622.094 094 8	−621.461 088 8
2,4-*t*-Bu$_2$PhOH	−619.833 415 3	−622.141 401 5	−621.497 729 5
2,5-*t*-Bu$_2$PhOH	−619.833 612 4	−622.142 240 4	−621.503 385 0
2,6-*t*-Bu$_2$PhOH	−619.826 712 7	−622.133 791 2	−621.502 445 6
3,4-*t*-Bu$_2$PhOH	−619.796 028 1	−622.106 815 8	−621.465 840 9
3,5-*t*-Bu$_2$PhOH	−619.834 536 3	−622.144 035 7	−621.501 336 5

Table 7. Calculated Bond Separation Energies at 0 K (BSE), Bond Separation Enthalpies at 298.15 K (BSH), and Experimental BSH Results for the Phenols (kJ·mol^{-1})

	MP2		DFT		exptl
compd	BSE	BSH	BSE	BSH	BSH
PhOH	352.63	371.99	325.59	344.95	321.8 ± 3.2
2-*t*-BuPhOH	416.68	447.58	341.41	372.31	372.5 ± 5.6
3-*t*-BuPhOH	416.90	448.76	349.32	381.18	385.8 ± 5.4
4-*t*-BuPhOH	416.09	447.23	347.85	378.99	375.1 ± 6.0
2,3-*t*-Bu$_2$PhOH	359.96	400.66	241.26	281.96	
2,4-*t*-Bu$_2$PhOH	479.08	523.76	365.46	410.14	433.5 ± 7.9
2,5-*t*-Bu$_2$PhOH	479.59	522.10	367.66	410.17	
2,6-*t*-Bu$_2$PhOH	461.48	504.99	345.48	388.99	422.2 ± 8.0
3,4-*t*-Bu$_2$PhOH	380.92	420.29	274.66	314.03	
3,5-*t*-Bu$_2$PhOH	482.02	526.52	372.38	416.87	

of the phenol molecules, through the energies associated to the following reactions:

$$C_6H_6O + 7CH_4 \rightarrow 3C_2H_4 + 3C_2H_6 + CH_3OH$$

$$C_{10}H_{14}O + 11CH_4 \rightarrow 3C_2H_4 + 7C_2H_6 + CH_3OH$$

$$C_{14}H_{22}O + 15CH_4 \rightarrow 3C_2H_4 + 11C_2H_6 + CH_3OH$$

These reactions were chosen to be of the isodesmic type; that is, the number of bonds of any formal type is conserved in each side of the equations and is likely to largely cancel the correlation errors in reactants and products, thus leading to reliable estimates of the reaction energies. The energies of these reactions represent in each case the stabilization of the aromatic phenol relative to the nondelocalized simpler molecules in the products side. The geometries of all auxiliary molecules were also optimized at the RHF/6-31G* level, and the resulting geometries were further used to obtain the MP2/6-31G* and DFT-NLSDA energies of the isodesmic reactions. The bond-separation energies, at 0 K, (BSE) and the bond-separation enthalpies, at 298 K, (BSH) for all the phenol molecules are collected in Table 7, together with the derived BSH values from the available experimental data. It can be seen from the results in Table 7 that both methods of calculation provide results predicting positive bond separation energies for all studied phenol molecules, indicating the occurrence of aromatic stabilization by electronic delocalization. The experimental stability ordering is well reproduced by both methods but is systematically overestimated by the MP2 results. On the other hand, DFT results seem much more confident as they are in much better agreement with experimental ones. Thus, we decided to use only DFT methods to continue our work. Although the comparisons of bond separation energies among molecules with different number of atoms is not significant, it can be observed from Table 7 that the introduction of the *tert*-butyl substituents leads to an increase of the bond separation energies, with the exception of the disubstituted 2,3- and 3,4-isomers, which, for steric reasons, show a decrease of the bond separation energy relative to nonsubstituted phenol.

Table 8. DFT Bond Separation Energies at 0 K (BSE) and Bond Separation Enthalpies at 298.15 K (BSH) for the Phenoxyl Radicals (kJ·mol^{-1})

compd	BSE	BSH
PhO$^\bullet$	382.12	397.20
2-*t*-BuPhO$^\bullet$	419.32	445.62
3-*t*-BuPhO$^\bullet$	416.48	444.22
4-*t*-BuPhO$^\bullet$	419.93	446.95
2,3-*t*-Bu$_2$PhO$^\bullet$	336.27	373.22
2,4-*t*-Bu$_2$PhO$^\bullet$	432.48	471.73
2,5-*t*-Bu$_2$PhO$^\bullet$	447.32	486.56
2,6-*t*-Bu$_2$PhO$^\bullet$	444.89	482.60
3,4-*t*-Bu$_2$PhO$^\bullet$	348.75	383.07
3,5-*t*-Bu$_2$PhO$^\bullet$	441.95	482.14

The relative stabilities of the phenoxyl radicals can, similarly, be estimated from the energy variation of isodesmic reactions analogous to the above ones:

$$C_6H_5O^\bullet + 7CH_4 \rightarrow 3C_2H_4 + 3C_2H_6 + CH_3O^\bullet$$

$$C_{10}H_{13}O^\bullet + 11CH_4 \rightarrow 3C_2H_4 + 7C_2H_6 + CH_3O^\bullet$$

$$C_{14}H_{21}O^\bullet + 15CH_4 \rightarrow 3C_2H_4 + 11C_2H_6 + CH_3O^\bullet$$

The resulting DFT/NSLDA bond separation energies at 0 K (BSE) and bond dissociation enthalpies at 298 K (BSH) for all radicals are collected in Table 8. The positive bond separation energies for the radicals show that all these species are stabilized by electronic delocalization. All isomers have positive bond separation energies, and the radicals have a greater stability when compared to the homologous closed-shell phenol molecules. This increasing of stability is enhanced by the introduction of the substituents, implying a corresponding weakening of the O−H bond.

The strength of the O−H bond has also been estimated as the O−H homolytic bond dissociation energy, at 0 K, D_e(O−H) (or the dissociation enthalpy, at 298.15 K, D_h(O−H)) defined as the energy (or enthalpy) associated to the following bond breaking reaction:

$$t\text{-Bu}_{1,2}\text{PhOH} \rightarrow t\text{-Bu}_{1,2}\text{PhO}^\bullet + \text{H}^\bullet$$

The results obtained from our DFT calculations are presented in Table 9. The introduction of the *tert*-butyl substituent (*t*-Bu) at the phenolic ring causes a systematic weakening of the O−H bond as antecipated above from the consideration of the bond-separation energies for the radicals and neutral species. This effect represents a weakening in a range from about 10 kJ mol^{-1} (for 3-*t*-Bu and 2,4-*t*-Bu$_2$PhOH) to about 40 kJ mol^{-1} (for 2,3-*t*-Bu$_2$ and 2,6-*t*-Bu$_2$PhOH).

The overall substituent weakening effect on the O−H bond dissociation energy of phenol can be quantitatively evaluated from the energy associated with the reaction

$$\text{PhO}^\bullet + t\text{-Bu}_{1,2}\text{PhOH} \rightarrow \text{PhOH} + t\text{-Bu}_{1,2}\text{PhO}^\bullet$$

which is just the difference between the O−H bond

Table 9. Calculated DFT and Experimental Homolytic O−H Bond Dissociation Energies (kJ·mol^{-1})

compd	D_e(O−H)	D_h(O−H)	$\Delta D_h(\mathrm{O-H})_{\mathrm{exp}}$[1]	ΔD_h(O−H)	$\Delta D_e(\mathrm{O-H})_{\mathrm{rad}}$	$\Delta D_e(\mathrm{O-H})_{\mathrm{phenol}}$
PhOH	391.96	363.65	0.0[a]	0.0	0.0	0.0
2-*t*-BuPhOH	370.58	342.62		−21.03	−13.71	7.66
3-*t*-BuPhOH	381.29	352.85		−10.80	−10.88	−0.24
4-*t*-BuPhOH	376.39	347.95	−7 ± 4	−15.70	−14.32	1.23
2,3-*t*-Bu_2PhOH	353.46	324.63		−39.02	−6.80	31.69
2,4-*t*-Bu_2PhOH	381.46	354.29	−22 ± 8	−9.36	−4.43	6.06
2,5-*t*-Bu_2PhOH	368.82	339.50		−24.15	−18.42	4.71
2,6-*t*-Bu_2PhOH	349.08	322.27	−26 ± 8	−41.38	−16.84	26.04
3,4-*t*-Bu_2PhOH	374.38	346.85		−16.80	−19.28	−1.71
3,5-*t*-Bu_2PhOH	378.90	350.61	−6 ± 4	−13.04	−13.90	−0.86

[a] $D_h(\mathrm{O-H})_{\mathrm{exp,}}$ phenol[1] = 371.3 ± 2.3 kJ·mol^{-1}.

dissociation energy of phenol and that of the substituted phenol. We can observe that our estimates of the O−H bond dissociation energies weakening $\Delta D_e(\mathrm{O-H})_{\mathrm{exp}}$ are in good agreement with the few available experimental results, $\Delta D_h(\mathrm{O-H})_{\mathrm{exp}}$. This weakening of the O−H bond may result either from a stabilization of the radical species upon substitution or from a destabilization of the closed-shell species, or even from a combination of both effects. The importance of each effect can be further evaluated from the energies for the reactions

$$\mathrm{PhOH} + t\text{-}\mathrm{Bu}_{1,2}\mathrm{C_6H_5} \rightarrow t\text{-}\mathrm{Bu}_{1,2}\mathrm{PhOH} + \mathrm{C_6H_6}$$

and

$$\mathrm{PhO}^{\bullet} + t\text{-}\mathrm{Bu}_{1,2}\mathrm{C_6H_5} \rightarrow t\text{-}\mathrm{Bu}_{1,2}\mathrm{PhO}^{\bullet} + \mathrm{C_6H_6}$$

representing, respectively, the stabilizing or destabilizing effect of the substituent *tert*-butyl on the phenol molecule and on the radical, both relative to its effect on benzene. The results of this analysis of substituent effect are presented in Table 9 under the columns $\Delta D_e(\mathrm{O-H})_{\mathrm{phenol}}$ and $\Delta D_e(\mathrm{O-H})_{\mathrm{rad}}$, respectively. The weakening of the O−H bond seems to result from a combined destabilization of the phenol molecule and stabilization of the corresponding radical, both measured relative to the effect the substituent has on benzene. We can easily infer that in the radicals the stabilizing effect of the substituent occurs always, and its magnitude covers a narrow range of about 4 kJ mol^{-1} to about 19 kJ mol^{-1}. On the other hand, the phenol molecules are almost always destabilized by the *tert*-butyl substitutents, with the exceptions of the 3-, 3,4-, and 3,5-isomers that, according to our calculations, are only marginally stabilized by the substituents. The destabilization of the phenol molecules spans a range of about 32 kJ mol^{-1}, thus being wider than the range of stabilization effects on the radicals. This wider range seems to result from greater sensitivity of the destabilization of the molecular phenols to the relative position of the substituents and the O−H group, reflecting the steric repulsions between the bulky *tert*-butyl substituents among themselves and with the O−H group.

Nevertheless, the global weakening effect is mainly dominated by the effect the substituent has on the radical species, the exceptions being specially the isomers with the substituents at the 2,3- and 2,6-positions. In these cases, the steric hindrance effect of the bulky *tert*-butyl groups, which are close to the O−H group, is evident and greatly contributes to unstabilize the neutral species; as a consequence, the weakening of the O−H bond is much more pronounced in these cases. For the 2,6-isomer the effects on the radical and on the closed-shell species have approximately the same magnitude.

In conclusion, we must note that DFT calculations performance allows a quite good reproduction of experimental findings relative to substituted phenols, mainly the homolytic O−H bond dissociation energies that are reproduced with errors that are within a 15 kJ mol^{-1} range. Although the calculated bond-separation energies reproduce the correct experimentally observed ordering, the quantitative agreement is only moderate in this case. In fact, while the calculated bond separation enthalpy of the monosubstituted phenols are in good agreement with experiment, those for the disubstituted isomers are underestimated by about 20−30 kJ mol^{-1}, and for nonsubstituted phenol an overestimation of ca. 20 kJ mol^{-1} is obtained. We have obseved a very similar behavior for the analogous subtituted benzenes.

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