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Thermochemical Parameters of the Chloronitrophenol Isomers: A Combined Experimental and Theoretical Investigation

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The standard ($p° = 0.1$ MPa) molar enthalpies of formation of 2-chloro-4-nitrophenol, 4-chloro-2-nitrophenol, and 4-chloro-3-nitrophenol in the solid phase, $\Delta_f H_m^\circ$(cr), at $T = 298.15$ K, were derived from the standard molar enthalpies of combustion measured by rotating-bomb combustion calorimetry, in oxygen. Enthalpies of fusion of the solid compounds were measured by differential scanning calorimetry. The standard molar enthalpies of sublimation, $\Delta_{cr}^{g} H_m^\circ$, at $T = 298.15$ K, were measured by Calvet microcalorimetry. Summing the obtained $\Delta_f H_m^\circ$(cr) and $\Delta_{cr}^{g} H_m^\circ$ values, it was possible to derive the values of the standard molar enthalpies of formation in the gaseous phase, at $T = 298.15$ K: $\Delta_f H_m^\circ$(2-chloro-4-nitrophenol, g) $= -(139.0 \pm 2.8)$ kJ·mol^{-1}, $\Delta_f H_m^\circ$(4-chloro-2-nitrophenol, g) $= -(149.2 \pm 1.8)$ kJ·mol^{-1}, and $\Delta_f H_m^\circ$(4-chloro-3-nitrophenol, g) $= -(108.8 \pm 3.7)$ kJ·mol^{-1}. Density functional theory calculations were also performed for all possible chloronitrophenol isomers using the B3LYP functional and the 6-31G** basis set. These calculations allowed the estimation of the standard molar enthalpies of formation in the gaseous phase for all isomers including those not studied experimentally. Identical DFT calculations were also carried out for the respective phenoxyl radicals and phenoxide anions which allowed the estimation of the O−H homolytic bond dissociation energies and gas-phase acidities.

Introduction

The present work is part of a wider study on the thermochemistry of substituted phenols, namely, *tert*-butyl- and di-*tert*-butylphenols,[1,2] cyanophenols,[3] methoxy- and dimethoxyphenols,[4] and methoxynitrophenols.[5] This family of compounds, the phenols, have a considerable practical interest because some of them have antioxidant properties which are directly related to the energetics of the O−H bond. There are many reports in the literature about the energetics of the phenolic bond;[6] nevertheless, values of standard enthalpies of formation for this family of compounds are still very scarce.[7] With this work we intend to enlarge the thermochemical database for substituted phenols by the experimental determination of the standard molar enthalpies of formation of some chloronitrophenol isomers and to use computational chemistry in the understanding of the relation between structure and energetics.

In this paper, we report the standard molar enthalpies of formation of three chloronitrophenol isomers, 2-chloro-4-nitrophenol (2-Cl-4-NO_2-C_6H_3OH), 4-chloro-2-nitrophenol (4-Cl-2-NO_2-C_6H_3OH), and 4-chloro-3-nitrophenol (4-Cl-3-NO_2-C_6H_3OH), in the gaseous phase, obtained from measurements of standard molar energies of combustion using a rotative bomb calorimeter and from the values of the standard molar enthalpies of sublimation measured by Calvet microcalorimetry.

In addition, density functional theory calculations were performed to obtain the most stable geometries for all possible chloronitrophenol isomers, respective phenoxyl radicals, and phenoxide anions. From these calculations, we obtained estimates of the standard molar enthalpies of formation in the gaseous phase for the chloronitrophenol isomers, including those not experimentally studied, the homolytic O−H bond dissociation energies, and the acidities in the gaseous phase.

Experimental Section

Materials and Purity Control. The chloronitrophenols were obtained commercially from Aldrich Chemical Co. with the minimum mass fraction purities: 0.97 for 2-Cl-4-NO_2-C_6H_3-OH CAS [619-08-9]; 0.98 for 4-Cl-2-NO_2-C_6H_3OH CAS [89-64-5]; 0.98 for 4-Cl-3-NO_2-C_6H_3OH CAS [610-78-6]. The three compounds were purified by repeated sublimation under reduced pressure, and their purity was assessed by differential scanning calorimetry (DSC) using the fractional fusion technique.[8] The mass fraction of impurities found was less than 1×10^{-3} for the three compounds. DSC experiments were performed on a Setaram DSC 141 calorimeter using a heating rate of 3.33×10^{-2} K·s^{-1}. The samples were hermetically sealed in stainless steel crucibles due to their high vapor pressure even at room temperature. The temperature scale of the calorimeter was calibrated by measuring the melting temperatures of three high-purity reference materials (naphthalene, benzoic acid, and indium), and its power scale was calibrated with high-purity indium (mass fraction >0.99999).[9]

The compositional purity of the compounds was further assessed by C, H, N, and Cl microanalyses. The specific density of the isomers was estimated as $\rho = 1.25$ g·cm^{-3}.

Combustion Calorimetry. The enthalpies of combustion were measured with an isoperibol rotating-bomb calorimeter. Because the apparatus and the technique have been described,[10,11] only a brief description of the apparatus will be given here. The bomb, whose internal volume is 0.337 dm^3, is lined with platinum. Water was added to the calorimeter from a weighed

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Perspex vessel, and for each experiment a correction to the energy equivalent was made for the deviation in the mass of water from 4063.3 g.

Calorimeter temperatures were measured to $\pm 10^{-4}$ K at time intervals of 10 s using a Hewlett-Packard (HP-2804A) quartz thermometer interfaced to a microcomputer, programmed to compute the adiabatic temperature change. For each experiment, the ignition temperature was chosen so that the final temperature would be close to $T = 298.15$ K. For both the fore-period and the after-period, 125 readings were taken, and for the main period, 100 readings were taken.

The rotating mechanism allowed simultaneous axial and end-over-end rotation of the bomb. Rotation of the bomb was started when the temperature rise in the main period reached about 0.63 of its total value and was continued throughout the rest of the experiment. By adopting this procedure, the frictional work due to the rotation of the bomb is automatically included in the temperature corrections for the work of water stirring and for the heat exchanged with the thermostatic jacket.[12]

The energy equivalent of the calorimeter was determined from the combustion of benzoic acid (Bureau of Analyzed Samples, Thermochemical Standard, BCS-CRM-190 r), having a specific energy of combustion, under certificate conditions, of $\Delta_c u = -(26\,432.3 \pm 3.8)\ \mathrm{J{\cdot}g^{-1}}$. Calibration experiments were carried out in oxygen at the pressure 3.04 MPa in the presence of 1.00 $\mathrm{cm^3}$ of water added to the bomb. One set of at least six calibration experiments was performed leading to the value of the energy equivalent of the calorimeter, $\epsilon(\text{calor.}) = (20\,680.6 \pm 1.7)\ \mathrm{J{\cdot}K^{-1}}$, where the uncertainty quoted is the standard deviation of the mean.

The three chloronitrophenols were burnt, in pellet form, in oxygen at the pressure 3.04 MPa, and an appropriate volume of an aqueous solution of As_2O_3 of known concentration was placed in the bomb to reduce to hydrochloric acid the free chlorine produced by the combustion.

The values of $\Delta_c H^\circ_m$ refer to the combustion reaction with $HCl{\cdot}600H_2O(l)$ as the chlorine-containing product in the final state. Within the precision of the analytical method, no evidence was found for oxidation of aqueous solution As_2O_3 during a time of about 5 h in the presence of oxygen at a pressure of 3.04 MPa.[13]

The solid pellet form of 4-chloro-2-nitrophenol was enclosed in melinex bags (as it is a volatile compound) using the technique described by Skinner and Snelson,[14] who determined the specific energy of combustion of dry melinex as $\Delta_c u^\circ = -(22\,902 \pm 5)\ \mathrm{J{\cdot}g^{-1}}$. This value was confirmed in our laboratory and used in this work. The mass of melinex used in each experiment was corrected for the mass fraction of water (0.0032), and the mass of carbon dioxide produced from it was calculated using the factor previously reported.[14]

The electrical energy for ignition was determined from the change in potential difference across a capacitor when discharged from 40 V through the platinum ignition wire. For the cotton thread fuse, with the empirical formula $CH_{1.686}O_{0.843}$, $\Delta_c u^\circ = -16\,250\ \mathrm{J\ g^{-1}}$.[15] This value was previously confirmed in our laboratory. The nitric acid formed was determined using Devarda's alloy method,[16] and the energetic corrections were based on $-59.7\ \mathrm{kJ{\cdot}mol^{-1}}$, for the molar energy of formation of $0.1\ \mathrm{mol{\cdot}dm^{-3}}$ $HNO_3(aq)$ from $N_2(g)$, $O_2(g)$, and $H_2O(l)$.[17]

The extent of the oxidation of $As_2O_3(aq)$ was determined by titration with a standardized iodine solution. The energy of oxidation of aqueous As_2O_3 to As_2O_5, $\Delta U(As_2O_3)$, was calculated as described by Hu et al.,[18] using the enthalpies of oxidation of $As_2O_3(aq)$ by Br_2 [19] and by Cl_2[20] and the thermal effects of mixing $As_2O_5(aq)$ with strong acids.[21] The amount of $H_2PtCl_6(aq)$ was determined from the loss of mass of platinum of the crucible, and the energy correction was based on $\Delta_f H^\circ_m(H_2PtCl_6,\ aq) = -(676.1 \pm 0.1)\ \mathrm{kJ{\cdot}mol^{-1}}$.[17] An estimated pressure coefficient of specific energy, $(\partial u/\partial p)_T = -0.2\ \mathrm{J{\cdot}g^{-1}{\cdot}MPa^{-1}}$ at $T = 298.15$ K, a typical value for most organic compounds, was assumed.[22] For each compound, the massic energy of combustion, $\Delta_c u^\circ$, was calculated by a procedure similar to that developed by Hubbard et al.[15] for compounds containing just C, H, and N and implemented by Hu et al.[18] for chlorine-containing compounds.

Microcalorimetry Calvet. The standard molar enthalpies of sublimation of the three chloronitrophenols were measured by Calvet microcalorimetry, using the vacuum sublimation drop microcalorimetric method.[23] Samples, about 3 to 5 mg of each crystalline compound, contained in small thin glass capillary tubes sealed at one end, were dropped, at room temperature, into the hot reaction vessel, in the high-temperature Calvet microcalorimeter (Calvet High-Temperature Microcalorimeter, SETARAM HT 1000) held at a convenient temperature of $T = 385$ K, and then removed from the hot zone by vacuum sublimation. Simultaneously, an empty capillary tube was dropped in the reference calorimetric cell. The observed enthalpies of sublimation, $\Delta^{g,T\mathrm{K}}_{cr,298.15\mathrm{K}} H^\circ_m$, were corrected to $T = 298.15$ K using the value of $\Delta^{T\mathrm{K}}_{298.15\mathrm{K}} H^\circ_m(g)$ estimated by a group method, on the basis of the values from Stull et al.[24] The microcalorimeter was calibrated in situ for these measurements making use of the recently recommended value of the standard molar enthalpy of sublimation, at $T = 298.15$ K, of naphthalene, $(72.600 \pm 0.600)\ \mathrm{kJ{\cdot}mol^{-1}}$.[25] Accuracy tests were performed with benzoic acid.

The relative atomic masses for the elements were those recommended by the IUPAC commission.[26]

Computational Details. Density functional theory calculations were carried out to obtain the most stable conformations of all possible chloronitrophenol isomers and their corresponding phenoxyl radicals and phenoxide anions as well using the Becke three-parameter hybrid exchange,[27] the Lee–Yang–Parr[28] correlation density functional (B3LYP), and the Poples split valence 6-31G** [29] basis set. Harmonic vibrational frequencies were calculated through construction and diagonalization of the Hessian matrices, using the same basis set. This procedure served both to characterize the obtained 6-31G** geometries as true minima and to obtain enthalpies at the temperature of 298.15 K. All calculations were performed using the U.K. version of GAMESS.[30,31]

Experimental Results

The enthalpies and temperatures of fusion of the crystalline 2-chloro-4-nitrophenol, 4-chloro-2-nitrophenol, and 4-chloro-3-nitrophenol were derived from the DSC experiments and are, respectively: 2-Cl-4-NO_2-C_6H_3OH, $\Delta^{l}_{cr} H^\circ_m(T_{fus}) = (20.88 \pm 0.15)\ \mathrm{kJ{\cdot}mol^{-1}}$, at $T_{fus} = (380.68 \pm 0.09)$ K; 4-Cl-2-NO_2-C_6H_3-OH, $\Delta^{l}_{cr} H^\circ_m(T_{fus}) = (22.69 \pm 0.13)\ \mathrm{kJ{\cdot}mol^{-1}}$, at $T_{fus} = (360.33 \pm 0.01)$ K; 4-Cl-3-NO_2-C_6H_3OH, $\Delta^{l}_{cr} H^\circ_m(T_{fus}) = (25.97 \pm 0.02)\ \mathrm{kJ{\cdot}mol^{-1}}$, at $T_{fus} = (399.44 \pm 0.09)$ K. The recorded thermograms did not show any phase transitions between 298 K and the melting temperature of the samples.

Determination of compositional purities was assessed by C, H, N, and Cl microanalyses. The results are presented in Table 1.

Results for a typical combustion experiment of each compound are given in Table 2, where $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from the mass

Table 1. Mass Fractions (*w*) of C, H, N, and Cl in the Chloronitrophenols

	calcd				found			
compd[a]	C	H	N	Cl	C	H	N	Cl
				w				
2-Cl-4-NO_2-C_6H_3OH	0.4152	0.0232	0.0807	0.2043	0.4172	0.0248	0.0799	0.2013
4-Cl-2-NO_2-C_6H_3OH	0.4152	0.0232	0.0807	0.2043	0.4151	0.0239	0.0802	0.2012
4-Cl-3-NO_2-C_6H_3OH	0.4152	0.0232	0.0807	0.2043	0.4165	0.0254	0.0786	0.2062

[a] Molar mass of $ClNO_2$-C_6H_3OH (M) = 173.556 g·mol^{-1}.

Table 2. Typical Combustion Results at T = 298.15 K[a]

	2-Cl-4-NO_2-C_6H_3OH	4-Cl-2-NO_2-C_6H_3OH	4-Cl-3-NO_2-C_6H_3OH
m(compound)/g	0.95304	1.07156	1.15380
m'(fuse)/g	0.00277	0.00279	0.00293
m''(melinex)/g		0.05597	
ΔT_{ad}/K	0.73577	0.88873	0.89604
ϵ_i/(J·K^{-1})	96.16	96.35	117.18
ϵ_f/(J·K^{-1})	94.12	94.27	114.55
$\Delta m(H_2O)$/g	2.5	0.2	0.6
$-\Delta U$(IBP)/J	15293.46	18464.65	18636.32
$-\Delta U$(fuse)/J	44.98	45.31	47.58
$-\Delta U$(melinex)/J		1281.82	
$-\Delta U(HNO_3)$/J	33.91	37.25	36.30
$-\Delta U(As_2O_3)$/J	223.58	249.18	295.00
$-\Delta U(H_2PtCl_6)$/J	0.31	0.60	0.20
$-\Delta U$(carbon)/J	0.00	0.00	0.00
ΔU(ign.)/J	1.20	1.19	1.19
$-\Delta U_\Sigma$/J	34.01	40.83	48.31
$-\Delta_c u°$(compound)/(J·g^{-1})	15693.64	15687.09	15781.70

[a] m(compound) is the mass of compound burnt in the experiment. m'(fuse) is the mass of fuse (cotton) used in the experiment. m''(melinex) is the mass of melinex used in the experiment. ΔT_{ad} is the corrected temperature rise. ϵ_i is the energy equivalent of contents in the initial state. ϵ_f is the energy equivalent of contents in the final state. $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from 4063.3 g; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; ΔU(IBP) includes ΔU(ign.). ΔU(fuse) is the energy of combustion of the fuse (cotton). ΔU(melinex) is the energy of combustion of the melinex. $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation. $\Delta U(As_2O_3)$ is the energy of oxidation of the aqueous solution of As_2O_3. $\Delta U(H_2PtCl_6)$ is the energy correction for the formation of the platinum complex. ΔU(carbon) is the energy correction for carbon formation. ΔU_Σ is the energy correction to the standard state. $\Delta_c u°$ is the standard massic energy of combustion.

assigned to ϵ(calor.). The remaining symbols in this table have the same meaning as in refs 15 and 18.

The internal energy for the isothermal bomb process, ΔU(IBP), was calculated according to the following equation:

$$\Delta U(\text{IBP}) = -\{\epsilon(\text{calor.}) + \Delta m(H_2O)c_p(H_2O, l)\}\Delta T_{ad} + \epsilon_i(T_i/K - 298.15) + \epsilon_f(298.15 - T_i/K - \Delta T_{ad}) + \Delta U_{ign.} \quad (1)$$

where ΔT_{ad} is the temperature change corrected for heat exchange with the surrounding thermostat and the work of stirring and of the bomb rotation.

The values of the massic energy of combustion, $\Delta_c u°$, refer to the combustion reaction

$$C_6H_4NO_3Cl(cr) + \frac{21}{4}O_2(g) + \frac{1197}{2}H_2O(l) \rightarrow 6CO_2(g) + HCl{\cdot}600H_2O(l) + \frac{1}{2}N_2(g) \quad (2)$$

with $HCl{\cdot}600H_2O(l)$ as the chlorine-containing product in the final state. The individual results of all combustion experiments, together with the mean value and its standard deviation, are given for each compound in Table 3. Table 4 lists the derived standard molar energies and enthalpies of combustion and the standard molar enthalpies of formation for the chloronitrophenols in the solid phase, at T = 298.15 K.

In accordance with normal thermochemical practice,[32] 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 and in the values of auxiliary quantities.

Table 3. Individual Values of the Massic Energy of Combustion, $\Delta_c u°$, at T = 298.15 K

	$-\Delta_c u°$/(J·g^{-1})	
2-Cl-4-NO_2-C_6H_3OH	4-Cl-2-NO_2-C_6H_3OH	4-Cl-3-NO_2-C_6H_3OH
15661.65	15685.78	15767.95
15684.93	15694.56	15785.36
15668.15	15696.99	15781.72
15683.78	15683.62	15790.58
15693.64	15675.89	15798.76
15682.76	15687.09	15788.65
15687.77		15781.70
	$-\langle\Delta_c u°\rangle$/(J·g^{-1})	
15680.4 ± 4.3	15687.3 ± 3.1	15785.0 ± 3.6

Table 4. Derived Standard Molar Values, at T = 298.15 K, of the Chloronitrophenols in the Crystalline Phase

	$\Delta_c U^\circ_m$(cr)	$\Delta_c H^\circ_m$(cr)	$\Delta_f H^\circ_m$(cr)
compd	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
2-Cl-4-NO_2-C_6H_3OH	−2721.4 ± 1.6	−2718.3 ± 1.6	−238.0 ± 1.8
4-Cl-2-NO_2-C_6H_3OH	−2722.6 ± 1.4	−2719.5 ± 1.4	−236.8 ± 1.6
4-Cl-3-NO_2-C_6H_3OH	−2739.6 ± 1.4	−2736.5 ± 1.4	−219.8 ± 1.6

To derive $\Delta_f H^\circ_m$(cr) from $\Delta_c H^\circ_m$(cr), the following standard molar enthalpies of formation, at T = 298.15 K, were used: H_2O(l), −(285.830 ± 0.042) kJ·mol^{-1};[33] CO_2(g), −(393.51 ± 0.13) kJ·mol^{-1};[33] and $\{HCl{\cdot}600H_2O(l) - 600H_2O(l)\}$, −(166.540 ± 0.005) kJ·mol^{-1}.[17,34]

The results of the measurements of the standard molar enthalpies of sublimation, $\Delta^g_{cr}H^\circ_m$, at T = 298.15 K, are given in Table 5 with uncertainties of twice the standard deviation of the mean. The derived standard molar enthalpies of formation, in both the crystalline and gaseous phases, for the three compounds are summarized in Table 6.

Table 5. Standard Molar Enthalpies of Sublimation of the Chloronitrophenols, at $T = 298.15$ K

compd	no. of exp.	T K	$\Delta_{\mathrm{cr},298.15\mathrm{K}}^{\mathrm{g},T\mathrm{K}} H_{\mathrm{m}}^{\circ}$ kJ·mol^{-1}	$\Delta_{298.15\mathrm{K}}^{T\mathrm{K}} H_{\mathrm{m}}^{\circ}(\mathrm{g})$ kJ·mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\circ}(298.15\ \mathrm{K})$ kJ·mol^{-1}
2-Cl-4-NO$_2$-C$_6$H$_3$OH	6	385	113.6 ± 2.1	14.6	99.0 ± 2.1
4-Cl-2-NO$_2$-C$_6$H$_3$OH	6	385	102.0 ± 0.9	14.6	87.6 ± 0.9
4-Cl-3-NO$_2$-C$_6$H$_3$OH	6	385	125.6 ± 3.3	14.6	111.0 ± 3.3

Table 6. Derived Standard Molar Enthalpies of Formation of the Chloronitrophenols, at $T = 298.15$ K

compd	$\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\circ}(\mathrm{cr})$ kJ·mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\circ}$ kJ·mol^{-1}	$\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\circ}(\mathrm{g})$ kJ·mol^{-1}
2-Cl-4-NO$_2$-C$_6$H$_3$OH	−238.0 ± 1.8	99.0 ± 2.1	−139.0 ± 2.8
4-Cl-2-NO$_2$-C$_6$H$_3$OH	−236.8 ± 1.6	87.6 ± 0.9	−149.2 ± 1.8
4-Cl-3-NO$_2$-C$_6$H$_3$OH	−219.8 ± 1.6	111.0 ± 3.3	−108.8 ± 3.7

Theoretical Results and Discussion

From the optimized geometries and the vibrational analysis of all isomers, we obtained, respectively, the B3LYP/6-31G** electronic energies and zero-point vibrational energies and thermal corrections to $T = 298.15$ K, which are presented in Table 7. To estimate the standard molar enthalpies of formation of the chloronitrophenols, we have considered the following isodesmic reaction:

$$C_6H_4NO_3Cl + 2C_6H_6 \rightarrow C_6H_5OH + C_6H_5NO_2 + C_6H_5Cl \quad (3)$$

The energy of this reaction is a measure of the interaction energy between the substituent groups in the aromatic ring, and it was chosen because the standard enthalpies of formation of all the auxiliary compounds—phenol −(96.4 ± 0.9) kJ·mol^{-1},[35] nitrobenzene (67.5 ± 0.8) kJ·mol^{-1},[35] chlorobenzene (52.0 ± 1.3) kJ·mol^{-1},[35] and benzene (82.6 ± 0.7) kJ·mol^{-1} [35]—are well-known experimentally. The electronic energies of all auxiliary molecules have been obtained using the same calculation procedure as that described for the chloronitrophenol isomers. The resultant reaction energies at $T = 0$ K, $\Delta_r E$, are reported in Table 8. To compare the theoretical with experimental results, the reaction enthalpies at $T = 298.15$ K, $\Delta_r H°$, were calculated from the reaction energies by adding the zero-point vibrational energies and the thermal corrections from $T = 0$ K to $T = 298.15$ K. The results for all isomers are also presented in Table 8, together with the derived standard enthalpies of formation, at $T = 298.15$ K, $\Delta_f H_m^\circ(\mathrm{g})$. The theoretical estimates of $\Delta_f H_m^\circ(\mathrm{g})$ are in good agreement with the experimentally observed values (Table 6), with a maximum deviation of 7 kJ·mol^{-1}. So, we may conclude that the theoretical estimates for the compounds not studied experimentally can be accepted with confidence. From the predicted values of the enthalpies of formation, we may conclude that the 5-chloro-2-nitrophenol is the most energetically stable isomer, whereas the 4-chloro-3-nitrophenol isomer is the most unstable one.

As it happens, with the monosubstituted chloro and nitrophenols, the most stable chloronitrophenol isomers are those in which the chlorine atom or the nitro group is close to the hydroxyl group. We can observe from the obtained 6-31G** optimized geometries that in the phenols substituted in the ortho position the hydroxyl group adopts a cis conformation relative to the chlorine atom or the nitro group, thus favoring the formation of an intramolecular hydrogen bond which represents a higher energetic stabilization of the isomer substituted in that position (see Table 7). The distance between the hydrogen atom of the hydroxyl group and the oxygen atom of the nitro group (0.167 to 0.169 nm) is smaller than the distance between the hydrogen atom of the hydroxyl group and the chlorine atom (0.236 to 0.241 nm). This could be due to a stronger intramolecular hydrogen bond and explains why in 2-chloro-6-nitrophenol the O−H bond adopts a cis conformation relative to the nitro group (the energy of the intramolecular hydrogen bond in 2-nitrophenol is 50.2 kJ·mol^{-1} and in chlorophenol is 13.2 kJ·mol^{-1} calculated from the energy difference between the cis and trans O−H conformations at the same level of theory, B3LYP/6-31G**).

With the purpose of studying the barrier height for internal rotation of the hydroxyl group, we have also performed geometry optimizations of the chloronitrophenols with the O−H bond frozen at 90° and all the other parameters optimized. In Table 9, we present the values of the energetic barriers for rotation around the C−O(H) bond, $\Delta_{\mathrm{rot}}E$ (estimated from the energies B3LYP/6-31G** obtained for the perpendicular (Table 7) and planar conformations), as well as the values of the barrier relative to phenol, $\Delta(\Delta_{\mathrm{rot}}E)$.

The results obtained for the phenols substituted in the ortho position are higher than those obtained for phenol and the other isomers, which confirms the existence of the intramolecular hydrogen bond. Nevertheless, the energetic barrier when the nitro group occupies the ortho position is higher than the barrier of those isomers where that position is occupied by the chlorine atom, which is due at least partially to the strong O−H···O intramolecular hydrogen bond. We have not found in the literature any experimental values for these barriers. The observation of the calculated energies suggests that the occurrence of the above-mentioned intramolecular hydrogen bond is the main factor determining the course stability ordering of chloronitrophenols. We can indeed roughly group these compounds into three classes: those having an *ortho*-nitro substituent are the most stable, immediately followed by those having an *ortho*-chlorine atom, and the isomers which don't have ortho substituents are the least stable

Other than this intramolecular stabilizing interaction, two other opposing "forces" come into play and can be invoked to make a fine-tuning of the relative stability order within each group. On one hand, there are stabilizing π-electronic delocalization effects between the aromatic π system and the three substituents. Actually, the hydroxyl group is a medium π-electron donor, the chlorine atom is a weak π-electron donor, and the nitro group is a strong π-electron acceptor, which are more efficient in the planar confomations. On the other hand, there are destabilizing electrostatic repulsions between substituents in neighboring positions which favor the nonplanar arrangement of one or more of the groups. These facts are evident from the dihedral angles which define the orientation of the substituent groups (see Figure 1 for the numbering of the atoms). The isomers 2-chloro-4-nitro-, 2-chloro-5-nitro-, 2-chloro-6-nitro-, 3-chloro-5-nitro-, 4-chloro-2-nitro-, and 5-chloro-2-nitrophenol are all planar molecules. This fact is also observed for phenol and the monosubstituted chloro and nitrophenols.[36−38] In the isomers 2-chloro-3-nitro- (dihedral angles: $C_2{-}C_3{-}N_{10}{-}O_{11}$ 38.6°; $C_4{-}C_3{-}N_{10}{-}O_{12}$ 39.1°), 3-chloro-4-nitro- (dihedral angles: $C_3{-}C_4{-}N_{10}{-}O_{11}$ 29.5°; $C_5{-}C_4{-}N_{10}{-}O_{12}$ 29.2°), and 4-chloro-3-nitrophenol (dihedral angles: $C_2{-}C_3{-}N_{10}{-}O_{11}$ 28.9°;

Table 7. Calculated B3LYP/6-31G Electronic Energies (hartree) and Zero-Point Vibrational Energies (kJ·mol^{-1}) of the Chloronitrophenols**

	molecule				radical			anion				perp.
	$E_{\mathrm{B3LYP/6-31G^{**}}}$	E_{ZP}	$E_{\mathrm{total}}{}^{a}$	$S_{\mathrm{total}}{}^{b}$	$E_{\mathrm{B3LYP/6-31G^{**}}}$	E_{ZP}	$E_{\mathrm{total}}{}^{a}$	$E_{\mathrm{B3LYP/6-31G^{**}}}$	E_{ZP}	$E_{\mathrm{total}}{}^{a}$	$S_{\mathrm{total}}{}^{b}$	$E_{\mathrm{B3LYP/6-31G^{**}}}$
C_6H_5OH	−307.478485	275.03	289.49	312.04	−306.835391	240.48	254.30	−306.892404	237.92	251.65	308.18	−307.472138
2-Cl-3-NO_2-C_6H_3OH	−971.560268	257.03	280.98	398.06	−970.910628	221.69	245.31	−971.008242	220.85	244.45	397.46	−971.549705
2-Cl-4-NO_2-C_6H_3OH	−971.574016	257.69	281.45	397.63	−970.922063	221.97	245.52	−971.038909	223.10	246.31	394.14	−971.562193
2-Cl-5-NO_2-C_6H_3OH	−971.571895	257.23	281.15	399.11	−970.921848	222.04	245.55	−971.023505	221.50	245.03	398.79	−971.562321
2-Cl-6-NO_2-C_6H_3OH	−971.576217	258.38	281.28	390.21	−970.911143	221.78	245.56	−971.022400	221.51	245.10	404.65	−971.556196
3-Cl-2-NO_2-C_6H_3OH	−971.565524	257.49	280.53	391.77	−970.906325	220.13	244.62	−971.009337	220.32	244.04	397.37	−971.549135
3-Cl-4-NO_2-C_6H_3OH	−971.560084	256.69	280.75	399.56	−970.909212	220.70	244.46	−971.025432	222.07	245.56	402.70	−971.552009
3-Cl-5-NO_2-C_6H_3OH	−971.569574	256.69	280.78	400.38	−970.919459	220.98	244.59	−971.023233	220.80	244.44	399.60	−971.562385
4-Cl-2-NO_2-C_6H_3OH	−971.578494	258.15	281.13	391.09	−970.914097	221.44	245.25	−971.022668	221.31	245.00	403.21	−971.557439
4-Cl-3-NO_2-C_6H_3OH	−971.557795	256.34	280.53	400.95	−970.911044	221.40	245.07	−971.007880	220.82	244.48	397.82	−971.550821
5-Cl-2-NO_2-C_6H_3OH	−971.580540	258.16	281.09	390.67	−970.910319	221.07	244.95	−971.025615	221.10	244.78	403.07	−971.557800

[a] E_{total} $(T = 298.15\ \mathrm{K}) = E_{\mathrm{trans}} + E_{\mathrm{rot}} + E_{\mathrm{ZP}} + \Delta_{0\mathrm{K}}^{298.15\mathrm{K}}E_{\mathrm{vib}}$. [b] S_{total} $(T = 298.15\ \mathrm{K}) = S_{\mathrm{trans}} + S_{\mathrm{rot}} + S_{\mathrm{vib}}$.

Table 8. Theoretical Estimates of the Standard Molar Enthalpies of Formation in the Gaseous Phase of the Chloronitrophenols, at T = 298.15 K (in kJ·mol^{-1})

	Δ_rE (T = 0 K)	$\Delta_rH°$ (T = 298.15 K)	$\Delta_fH_m^\circ$(g)	$\Delta_fH_m^\circ$(g) exptl
2-Cl-3-NO_2-C_6H_3OH	−33.6	−33.5	−108.6	
2-Cl-4-NO_2-C_6H_3OH	2.5	2.1	−144.2	−139.0 ± 2.8
2-Cl-5-NO_2-C_6H_3OH	−3.0	−3.1	−139.0	
2-Cl-6-NO_2-C_6H_3OH	8.3	8.1	−150.2	
3-Cl-2-NO_2-C_6H_3OH	−19.8	−19.2	−122.9	
3-Cl-4-NO_2-C_6H_3OH	−34.0	−33.8	−108.3	
3-Cl-5-NO_2-C_6H_3OH	−9.1	−8.9	−133.2	
4-Cl-2-NO_2-C_6H_3OH	14.3	14.2	−156.3	−149.2 ± 1.8
4-Cl-3-NO_2-C_6H_3OH	−40.0	−39.5	−102.6	−108.8 ± 3.7
5-Cl-2-NO_2-C_6H_3OH	19.7	19.6	−161.7	

Table 9. Energetic Barrier for Rotation of the O−H Bond

compd	$\Delta_{\mathrm{rot}}E$ kJ·mol^{-1}	$\Delta(\Delta_{\mathrm{rot}}E)$ kJ·mol^{-1}
C_6H_5OH	16.7	0.0
2-Cl-3-NO_2-C_6H_3OH	27.7	11.1
2-Cl-4-NO_2-C_6H_3OH	31.0	14.3
2-Cl-5-NO_2-C_6H_3OH	25.1	8.5
2-Cl-6-NO_2-C_6H_3OH	52.6	35.9
3-Cl-2-NO_2-C_6H_3OH	43.0	26.4
3-Cl-4-NO_2-C_6H_3OH	21.2	4.5
3-Cl-5-NO_2-C_6H_3OH	18.9	2.2
4-Cl-2-NO_2-C_6H_3OH	55.3	38.6
4-Cl-3-NO_2-C_6H_3OH	18.3	1.6
5-Cl-2-NO_2-C_6H_3OH	59.7	43.0

C_4−C_3−N_{10}−O_{12} 29.6°), the steric repulsions between adjacent groups are minimized by the nonplanar arrangement of the nitro group, and in the 3-chloro-2-nitrophenol (dihedral angles: C_2−C_1−O_7−H_8 10.5°; C_1−C_2−N_{10}−O_{11} 24.4°; C_3−C_2−N_{10}−O_{12} 25.0°), the steric repulsions are minimized by the nonplanar arrangement of both the hydroxyl and nitro groups.

The homolytic O−H bond dissociation energy (T = 0 K), D_e(O−H), and the corresponding bond dissociation enthalpy (T = 298.15 K), D_h(O−H), defined, respectively, as the energy and enthalpy variations associated with the following bond-breaking reactions

$$\text{Cl-NO}_2\text{-C}_6\text{H}_3\text{O-H} \rightarrow \text{Cl-NO}_2\text{-C}_6\text{H}_3\text{-O}^\bullet + \text{H}^\bullet \qquad (4)$$

were calculated, and the results are collected in Table 10. In agreement with Brinck et al.,[39] our calculations predict the value of 346.0 kJ·mol^{-1} for the homolytic O−H bond dissociation enthalpy of phenol. This value is about 25 kJ·mol^{-1} lower than the selected experimental value of (371.3 ± 2.3) kJ·mol^{-1}.[6] Despite the consistent failure of the B3LYP functional in the determination of accurate O−H bond dissociation enthalpies,[40] it is known that the relative values ΔD_h(O−H) are found to be in good agreement with the experimental data and with more sophisticated computational methods.[41−43] In the case of the chloronitrophenol isomers, there are no experimental ΔD_h(O−H) values for comparison with our theoretical results.

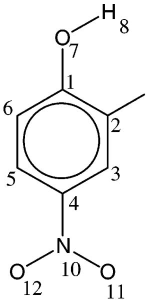

Figure 1. Atom numbering scheme for the chloronitrophenols.

The effect of the introduction of the two substituents is to strengthen the O−H bond in respect to the homolytic bond-breaking processes, the calculated increase of ΔD_h(O−H) ranging from about 9.3 kJ·mol^{-1} (4-chloro-3-nitrophenol) to 70.3 kJ·mol^{-1} (5-chloro-2-nitrophenol). The overall substituent effect on the O−H bond dissociation energy can be usefully partitioned into the effect the substituent has in the radicals (radical contribution, rc) and its effect in the closed-shell molecules (parent contribution, pc). The importance of each effect can be evaluated from the energy variation of the reactions

$$\text{C}_6\text{H}_5\text{NO}_2 + \text{C}_6\text{H}_5\text{Cl} + \text{C}_6\text{H}_5\text{OH} \rightarrow \text{Cl-NO}_2\text{-C}_6\text{H}_3\text{OH} + 2\text{C}_6\text{H}_6 \qquad (5)$$

$$\text{C}_6\text{H}_5\text{NO}_2 + \text{C}_6\text{H}_5\text{Cl} + \text{C}_6\text{H}_5\text{O}^\bullet \rightarrow \text{Cl-NO}_2\text{-C}_6\text{H}_3\text{-O}^\bullet + 2\text{C}_6\text{H}_6 \qquad (6)$$

which represent, respectively, the effect of the substituents on the stability of the closed-shell molecule and of the radicals, both measured relative to its effect on benzene. The results of this analysis are also presented in Table 10 under the headings $\Delta^{\mathrm{pc}}D_e$(O−H) and $\Delta^{\mathrm{rc}}D_e$(O−H). It can be observed from these results that all phenoxyl radicals are destabilized by the substituents, and on the other hand, the closed-shell molecules are either stabilized or destabilized.

For a better understanding of the effect of the entrance of both substituents, we have performed similar calculations for the monosubstituted chloro and nitrophenols, and the results are also presented in Table 10. The theoretical B3LYP/6-31G** estimates of ΔD_h(O−H) reproduce and are quantitatively in agreement with the recommended values, except for the 2-nitrophenol isomer. There is a large discrepancy between our calculated value and the recommended value for this isomer.

Table 10. Calculated Homolytic O−H Bond Dissociation Energies (kJ·mol^{-1})

			ΔD_h(O−H)					
compd	D_e(O−H)	D_h(O−H)		(6)	(42)	(43)	$\Delta^{pc}D_e$	$\Delta^{rc}D_e$
C_6H_5OH	375.0	346.0	0.0	0.0	0.0	0.0	0.0	0.0
2-Cl-C_6H_4OH	382.6	353.6	7.6	−3 ± 4		5.4	4.2	−3.4
3-Cl-C_6H_4OH	379.9	350.5	4.5	5 ± 4	3.8	5.0	−0.7	−5.7
4-Cl-C_6H_4OH	372.0	343.1	−2.9	−1 ± 4	−5.9	−6.3	−2.3	0.7
2-NO_2-C_6H_4OH	436.7	406.6	60.0	−5 ± 8		50.6	24.9	−36.8
3-NO_2-C_6H_4OH	389.6	359.9	13.9	19 ± 8	13.4	14.2	0.0	−14.6
4-NO_2-C_6H_4OH	393.5	363.6	17.6	25 ± 8	17.6	19.2	5.8	−12.7
2-Cl-3-NO_2-C_6H_3OH	392.2	362.7	16.7				−33.6	−50.7
2-Cl-4-NO_2-C_6H_3OH	398.2	368.5	22.5				2.5	−20.7
2-Cl-5-NO_2-C_6H_3OH	393.2	363.8	17.9				−3.0	−21.3
2-Cl-6-NO_2-C_6H_3OH	432.7	403.2	57.2				8.3	−49.4
3-Cl-2-NO_2-C_6H_3OH	417.3	387.6	41.6				−19.8	−62.0
3-Cl-4-NO_2-C_6H_3OH	395.4	365.3	19.3				−34.0	−54.5
3-Cl-5-NO_2-C_6H_3OH	393.4	363.4	17.4				−9.1	−27.6
4-Cl-2-NO_2-C_6H_3OH	430.9	401.2	55.2				14.3	−41.6
4-Cl-3-NO_2-C_6H_3OH	384.6	355.3	9.3				−40.0	−49.6
5-Cl-2-NO_2-C_6H_3OH	446.2	416.3	70.3				19.7	−51.6

Table 11. Calculated Gas-Phase Acidities (kJ·mol^{-1})

			$\Delta(\Delta_{acid}G°)$			
compd	$\Delta_{acid}E$(O−H)	$\Delta_{acid}G°$		(46)	(48)	$\Delta^{ac}D_e$
C_6H_5OH	1538.8	1475.8	0.0	0.0	0.0	0.0
2-Cl-C_6H_4OH	1507.7	1444.6	−31.2		−3.6	35.3
3-Cl-C_6H_4OH	1498.2	1435.4	−40.4	−29.7	0.8	39.8
4-Cl-C_6H_4OH	1503.5	1441.0	−34.8	−24.7	2.3	32.9
2-NO_2-C_6H_4OH	1489.5	1423.3	−52.5		−58.2	74.2
3-NO_2-C_6H_4OH	1468.9	1406.3	−69.5	−60.2	−65.7	69.9
4-NO_2-C_6H_4OH	1426.8	1366.9	−108.9	−87.4	−107.9	117.8
2-Cl-3-NO_2-C_6H_3OH	1449.3	1386.7	−89.1			55.9
2-Cl-4-NO_2-C_6H_3OH	1404.9	1344.5	−131.2			136.4
2-Cl-5-NO_2-C_6H_3OH	1439.8	1377.5	−98.3			95.9
2-Cl-6-NO_2-C_6H_3OH	1454.0	1387.3	−88.5			93.0
3-Cl-2-NO_2-C_6H_3OH	1460.3	1395.8	−80.0			58.7
3-Cl-4-NO_2-C_6H_3OH	1403.7	1341.3	−134.5			101.0
3-Cl-5-NO_2-C_6H_3OH	1434.4	1372.0	−103.8			95.2
4-Cl-2-NO_2-C_6H_3OH	1459.3	1393.3	−82.5			93.7
4-Cl-3-NO_2-C_6H_3OH	1443.8	1382.4	−93.4			54.9
5-Cl-2-NO_2-C_6H_3OH	1457.0	1390.7	−85.1			101.5

However, we must note that the recommended value is based on two different values of the enthalpy of dissociation, $\Delta D_h(O-CH_3)$, of 1-nitro-2-methoxybenzene (an estimate of −5.4 kJ·mol^{-1} was based on *very low-pressure pyrolysis* experiments,[44,45] and the other (10.9 kJ·mol^{-1}) is based on theoretical AM1 calculations[44,45]). This fact makes meaningless the comparison in this case because in phenols, but not in anisoles, intramolecular hydrogen bonds can be formed between the OH and the substituent, thereby stabilizing the parent molecule. This same fact was also observed for the cyanophenol isomers.[3] A discrepancy is also found here for the chloro substitution, and a similar explication can be given. The good quality of the results obtained for the closed-shell systems (Table 8) allows us to believe that the values obtained in the present work are more reliable.

The effect of the chlorine atom on the O−H bond dissociation energy is small and irregular. The nitro group induces an increase of the bond dissociation enthalpy of phenol. All phenoxyl radicals are destabilized by the nitro group, a fact that can be explained by observing that the oxygen atom of the phenoxyl radical is a strong π-electron acceptor, thus being destabilized by the nitro group which is also a strong π-electron acceptor. On the other hand, the closed-shell molecules are stabilized by the nitro substituent. The dominant effect in the increase of the O−H bond dissociation energy is the destabilizing effect of the substituent groups on the phenoxyl radicals. On the other hand, the effect on the closed-shell molecules is small. So, we may conclude that the calculated increase of ΔD_h(O−H) for the chloronitrophenols is mainly due to the nitro substituent.

The absolute gas-phase acidity of the chloronitrophenols, at $T = 298.15$ K, defined as the Gibbs function variation for the following heterolytic bond-breaking reaction

$$\text{Cl-NO}_2\text{-C}_6\text{H}_3\text{OH} \rightarrow \text{Cl-NO}_2\text{-C}_6\text{H}_3\text{-O}^- + \text{H}^+ \tag{7}$$

has also been estimated from the thermodynamic equation $\Delta_{acid}G° = \Delta_{acid}H° - T\Delta_{acid}S°$ ($\Delta_{acid}S°$ was obtained using standard statistical thermodynamics formulas), and the results are shown in Table 11. We can observe from that table that the introduction of the two substituents leads to an increase in the acidity that varies from 80.0 kJ·mol^{-1} (3-chloro-2-nitrophenol) to 134.5 kJ·mol^{-1} (3-chloro-4-nitrophenol).

The B3LYP/6-31G** theoretical estimate of the gas-phase acidity of phenol, 1472.1 kJ·mol^{-1}, is considerably higher than the experimental values (1432.0 ± 8.4) kJ·mol^{-1} [46] and (1437.0 ± 8.4) kJ·mol^{-1} [47] recommended in a compilation by Bartmess.[49] In the same compilation, we have found the value of the gas-phase acidity of 2-chloro-4-nitrophenol (1323 ± 8.4) kJ·mol^{-1}.

A partitioning of the overall substituent effect on the O−H heterolytic bond dissociation energy into the effect of the substituent in the closed-shell molecules and the effect in the anion (anion contribution, ac) can be obtained similarly to what has been done for the homolytic bond-breaking processes by using the additional reaction

$$\text{C}_6\text{H}_5\text{NO}_2 + \text{C}_6\text{H}_5\text{Cl} + \text{C}_6\text{H}_5\text{O}^- \rightarrow \text{Cl-NO}_2\text{-C}_6\text{H}_3\text{-O}^- + 2\text{C}_6\text{H}_6 \tag{8}$$

whose energy variation represents the effect of the substituents on the anion, measured relative to its effect on benzene. The individual contributions are also shown in Table 11 under the heading $\Delta^{ac}D_e$(O−H). A similar study was also performed for the monosubstituted chloro and nitrophenols.

The most obvious result which can be observed is that the effect of the substituents on the acidity is largely determined by the effect of the substituents in the anionic species and only to a little extent in the corresponding closed-shell system. The π-electron acceptor nitro group interacts favorably with the π donor oxygen atom of the phenoxide anion when it is situated at the ortho and para positions, the result being an enhanced delocalization of the negative charge of the oxygen atom. This interaction stabilizes the anionic species and reveals to be more effective when both substituents occupy mutual para positions.

Anions are mostly stabilized by the same mechanism, which determines the stabilization of their closed-shell counterparts. The main difference is that the interaction of the substituent $-NO_2$ with O^- is considerably stronger than with $-OH$. From Table 11, we can observe that although the former interaction energies vary from 54.9 $kJ \cdot mol^{-1}$ to 136.4 $kJ \cdot mol^{-1}$ the latter are just in the range 0 to -8 $kJ \cdot mol^{-1}$, thus giving support to the conjecture that the substituent effects on the heterolytic O−H bond dissociation energy of phenols are mainly due to the interactions which occur in anionic systems.

Literature Cited

(1) Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Morais, V. M. F.; Miranda, M. S. Thermochemical and Theoretical Study of *tert*-Butyl and Di-*tert*-butylphenol Isomers. *J. Org. Chem.* **1999**, *64*, 8816−8820.

(2) Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Miranda, M. S.; Sousa, M. H. F. A.; Santos, R. M. B.; Bizarro, M. M.; Simões, J. A. M. Standard Enthalpies of Formation of 2,6-Di-*Tert*-butyl-4-methylphenol and 3,5-Di-*Tert*-butylphenol and their Phenoxy Radicals. *Struct. Chem.* **2001**, *12*, 171−181.

(3) Matos, M. A. R.; Miranda, M. S.; Morais, V. M. F. Thermochemical Study of the Cyanophenol Isomers. *Struct. Chem.* **2004**, *15*, 99−112.

(4) Matos, M. A. R.; Miranda, M. S.; Morais, V. M. F. Thermochemical Study of the Methoxy- and Dimethoxyphenol Isomers. *J. Chem. Eng. Data* **2003**, *48*, 669−679.

(5) Miranda, M. S.; Morais, V. M. F.; Matos, M. A. R. Standard Molar Enthalpies of Formation of the Methoxynitrophenol Isomers: a Combined Experimental and Theoretical Investigation. *J. Chem. Thermodyn.* **2004**, *36*, 431−436.

(6) Santos, R. M. B.; Simões, J. A. M. Energetics of the O−H Bond in Phenol and Substituted Phenols: A Critical Evaluation of Literature Data. *J. Phys. Chem. Ref. Data* **1998**, *27*, 707−741.

(7) Slayden, S. W.; Liebman, J. F. Thermochemistry of Phenols and Related Arenols. In *The Chemistry of Phenols*; Rappoport, Z., Ed.; Wiley: Chichester, 2003; pp 223−257.

(8) Plato, C.; Glasgow, A. R., Jr. Differential Scanning Calorimetry as a General Method for Determining Purity and Heat of Fusion of High-Purity Organic Chemicals. Application to 95 Compounds. *Anal. Chem.* **1969**, *41*, 330−336.

(9) Sabbah, R.; Xu-wu, A.; Chickos, J. S.; Leitão, M. L. P.; Roux, M. V.; Torres, L. A. Reference Materials for Calorimetry and Differential Thermal Analysis. *Thermochim. Acta* **1999**, *331*, 93−204.

(10) Cox, J. D.; Gundry, H. A.; Head, A. Thermodynamic Properties of Fluorine Compounds. Heats of Combustion of *p*-Fluorobenzoic Acid, Pentafluorobenzoic Acid, Hexafluorobenzene and Decafluorocyclohexene. *Trans. Faraday Soc.* **1964**, *60*, 653−665.

(11) Ribeiro da Silva, M. A. V.; Gonçalves, J. M.; Pilcher, G. Standard Molar Enthalpies of Formation of Nine Fluorinated β-Diketones by Rotating Bomb Calorimetry. *J. Chem. Thermodyn.* **1997**, *29*, 253−260.

(12) Good, W. D.; Scott, D. W.; Waddington, G. Combustion Calorimetry of Organic Fluorine Compounds by a Rotating-Bomb Method. *J. Phys. Chem.* **1956**, *60*, 1080−1089.

(13) Ribeiro da Silva, M. A. V.; Ferrão, M. L. C. C. H.; Fang, J. Standard Enthalpies of Combustion of the 6 Dichlorophenols by Rotating-Bomb Calorimetry. *J. Chem. Thermodyn.* **1994**, *26*, 839−846.

(14) Skinner, H. A.; Snelson, A. The Heats of Combustion of the Four Isomeric Butyl Alcohols. *Trans. Faraday Soc.* **1960**, *56*, 1776−1783.

(15) Hubbard, W. N.; Scott, D. W.; Waddington, G. Standard States and Corrections for Combustions in a Bomb at Constant Volume. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol. 1, Chapter 5.

(16) Vogel, A. I. *Quantitative Inorganic Analysis*; Longman: London, 1978.

(17) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nutall, R. L. The NBS Tables of Chemical Thermodynamic Properties. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2.

(18) Hu, A. T.; Sinke, G. C.; Ringnér, B.; Mansson, M. Test Substances for Bomb Combustion Calorimetry − para Chlorobenzoic Acid. *J. Chem. Thermodyn.* **1972**, *4*, 283−299.

(19) Bjellerup, L.; Sunner, S.; Wadso, I. The Heat of Oxidation of Arsenious Oxide to Arsenic Oxide in Aqueous Solution. *Acta Chem. Scand.* **1957**, *11*, 1761−1765.

(20) Sunner, S.; Thorén, S. Heat of Oxidation of Aqueous Arsenious Oxide with Gaseous Chlorine. *Acta Chem. Scand.* **1964**, *18*, 1528−1532.

(21) Sellers, P.; Sunner, S.; Wadso, I. Heats of Ionization of Arsenious + Arsenic Acids. *Acta Chem. Scand.* **1964**, *18*, 202−206.

(22) Washburn, E. W. Standard States for Bomb Calorimetry. *J. Res. Natl. Bur. Stand. (U.S.)* **1933**, *10*, 525−558.

(23) Adedeji, F. A.; Brown, D. L. S.; Connor, J. A.; Leung, M. L.; Paz-Andrade, I. M.; Skinner, H. A. Thermochemistry of Arene Chromium Tricarbonyls and the Strengths of Arene−Chromium Bonds. *J. Organomet. Chem.* **1975**, *97*, 221−228.

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

(25) Chickos, J. S.; Acree, W. E., Jr. Enthalpies of Sublimation of Organic and Organometallic Compounds. 1910−2001. *J. Phys. Chem. Ref. Data* **2002**, *31*, 537−698.

(26) Coplen, T. B. Atomic Weights of the Elements 1999. *J. Phys. Chem. Ref. Data* **2001**, *30*, 701−712.

(27) Becke, A. D. Density-Functional Thermochemistry. 3. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(28) Lee, C. T.; Yang, W. T.; Parr, R. G. Development of the Colle−Salvetti Correlation Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785−789.

(29) Hariharan, P. C.; Pople, J. A. Influence of Polarization Functions on Molecular-Orbital Hydrogenation Energies. *Theor. Chim. Acta* **1973**, *28*, 213−222.

(30) GAMESS-UK is a package of ab initio programs written by Guest, M. F.; van Lenthe, J. H.; Kendrick, J.; Schoffel, K.; and Sherwood, P., with contributions from Amos, R. D.; Buenker, R. J.; van Dam, H. J. J.; Dupuis, M.; Handy, N. C.; Hillier, I. H.; Knowles, P. J.; Bonacic-Koutecky, V.; von Niessen, W.; Harrison, R. J.; Rendell, A. P.; Saunders, V. R.; Stone, A. J.; and de Vries, A. H. The package is derived from the original GAMESS code due to: Dupuis, M.; Spangler, D.; Wendoloski, J. *NRCC Software Catalog*; Program No. QG01 (GAMESS), 1980; Vol. 1.

(31) The DFT module within GAMESS-UK was developed by Dr. P. Young under the auspices of EPSRC's Collaborative Computacional Project No. 1 (CCP1) (1995−1997).

(32) Rossini, F. D. Assignment of Uncertainties to Thermochemical Data. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol. 1, Chapter 14.

(33) CODATA Recommended Key Values for Thermodynamics, 1977. Report of the CODATA Task Group on Key Values for Thermodynamics. *J. Chem. Thermodyn.* **1978**, *10*, 903−906.

(34) Cox, J. D., Wagman, D. D., Medvedev, V. A., Eds. *CODATA Key Values for Thermodynamics*; Hemisphere: New York, 1989.

(35) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; TRC Data Series; College Station: Texas, 1994.

(36) Larsen, N. W. Microwave Spectra of the 6 Mono-C-13-Substituted Phenols and of Some Mono-Deuterated Species of Phenol-Complete Substitution Structure and Absolute Dipole Moment. *J. Mol. Struct.* **1979**, *51*, 175−190.

(37) Chen, P. C.; Lo, W.; Tzeng, S. C. Molecular Structures of Mononitrophenols and their Thermal Decomposition Tautomers. *J. Mol. Struct. (Theochem)* **1998**, *428*, 257−266.

(38) Borisenko, K. B.; Bock, C. W.; Hargittai, I. Intramolecular Hydrogen Bonding and Molecular Geometry of 2-Nitrophenol from a Joint Gas-Phase Electron Diffraction and ab Initio Molecular Orbital Investigation. *J. Phys. Chem.* **1994**, *98*, 1442−1448.

(39) Brinck, T.; Haeberlein, M.; Jonsson, M. A Computational Analysis of Substituent Effects on the O−H Bond Dissociation Energy in Phenols: Polar versus Radical Effects. *J. Am. Chem. Soc.* **1997**, *119*, 4239−4244.

(40) Guedes, R. C.; Cabral, B. J. C.; Simões, J. A. M.; Diogo, H. P. Thermochemical Properties and Structure of Phenol−$(H_2O)_{1-6}$ and Phenoxy−$(H_2O)_{(1-4)}$ by Density Functional Theory. *J. Phys. Chem. A* **2000**, *104*, 6062−6068.

(41) Wright, J. S.; Carpenter, D. J.; McKay, D. J.; Ingold, K. U. Theoretical Calculation of Substituent Effects on the O−H Bond Strength of Phenolic Antioxidants Related to Vitamin E. *J. Am. Chem. Soc.* **1997**, *119*, 4245−4252.

(42) Chandra, A. K.; Uchimaru, T. The O−H Bond Dissociation Energies of Substituted Phenols and Proton Affinities of Substituted Phenoxide Ions: A DFT Study. *Int. J. Mol. Sci.* **2002**, *3*, 407−422.

(43) Wright, J. S.; Johnson, E. R.; DiLabio, G. A. Predicting the Activity of Phenolic Antioxidants: Theoretical Method, Analysis of Substituent Effects, and Application to Major Families of Antioxidants. *J. Am. Chem. Soc.* **2001**, *123*, 1173−1183.

(44) Suryan, M. M.; Kafafi, S. A.; Stein, S. E. The Thermal Decomposition of Hydroxy-Substituted and Methoxy-Substituted Anisoles. *J. Am. Chem. Soc.* **1989**, *111*, 1423−1429.

(45) Suryan, M. M.; Kafafi, S. A.; Stein, S. E. Dissociation of Substituted Anisoles. Substituent Effects on Bond Strengths. *J. Am. Chem. Soc.* **1989**, *111*, 4594−4600.

(46) Fujio, M.; McIver, R. T., Jr.; Taft, R. W. Effects on the Acidities of Phenols from Specific Substituent−Solvent Interactions. Inherent

Substituent Parameters from Gas-Phase Acidities. *J. Am. Chem. Soc*. **1981**, *103*, 4017−4029.

(47) Cumming, J. B.; Kebarle, P. Summary of Gas-Phase Acidity Measurements Involving Acids AH. Entropy Changes in Proton-Transfer Reactions Involving Negative Ions. Bond Dissociation Energies D(A-H) and Electron Affinities EA(A). *Can. J. Chem*. **1978**, *56*, 1−9.

(48) McMahon, T. B.; Kebarle, P. Intrinsic Acidities of Substituted Phenols and Benzoic Acids Determined by Gas-Phase Proton-Transfer Equilibria. *J. Am. Chem. Soc.* **1977**, *99*, 2222−2230.

(49) Bartmess, J. E. Negative Ion Energetics Data. In *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Tecnology: Gaithersburg, MD 20899, March 2003 (http://webbook.nist.gov).

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