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Ab Initio Studies on Acid−Base Equilibria of Substituted Phenols

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By using ab initio methods at the RHF and MP2 levels, as well as the PCM model utilizing the Gaussian 6-31++G** basis set, we calculated energies and Gibbs free energies of protonation and formation of homocomplexed anions stabilized by O···H···O bridges for 10 substituted phenol systems in the gas phase and after consideration of solvation energies in solution. The calculated protonation energies, ΔE_{prot}, and Gibbs free energies, ΔG_{prot}, have been found to correlate well with the acid dissociation constants in acetonitrile (AN) solutions (expressed as $\mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}}$ values). The energies, $\Delta E_{\mathrm{AHA^-}}$, and Gibbs free energies, $\Delta G_{\mathrm{AHA^-}}$, of anionic homoconjugation do not correlate well with the experimental anionic homoconjugation constant values determined in acetonitrile.

Introduction

This work is a continuation of studies concerning acid−base interactions, which were carried out in our group, using experimental[1−4] and theoretical methods.[5−9] A model of acid−base equilibria, which can be observed between phenol and its derivatives in organic solvents, is highly complex.[10] Nevertheless, this model can be predicted and limited, under experimental conditions, to so-called fundamental equilibria only, those of protonation of anionic base (eq 1), as well as anionic homoconjugation (eq 2):

$$\mathrm{A^- + H^+ \rightleftarrows HA} \tag{1}$$

$$\mathrm{HA + A^- \rightleftarrows AHA^-} \tag{2}$$

where $\mathrm{A^-}$ denotes the anionic base, HA is an acid conjugated with base $\mathrm{A^-}$, and $\mathrm{AHA^-}$ denotes a symmetric homocomplexed anion. These equilibria (eqs 1 and 2) have been the main objects of our interests in this work.

In our previous papers[11,12] some experimental studies of acid−base properties of the phenol−phenolate systems in acetonitrile and dimethyl sulfoxide were carried out. It was found that the phenol and its derivatives have a high tendency toward hydrogen-bonding systems formation. This is of high importance because they can be used to model the side-chain of tyrosine, which is one of the amino acids found in living systems. The hydrogen-bond formation in side-chains of biomolecules can potentially stabilize the protein structure.

The above-mentioned interesting features of the family of organic proton donors prompted us to undertake investigations into their acid−base properties. By using ab initio methods, energetic parameters (energies and Gibbs free energies) of protonation and formation of the homocomplexed anions in 10 acid−base systems formed by phenol and its substituted derivatives were determined in the gaseous phase at both the restricted Hartree−Fock (RHF) and the Møller−Plesset (MP2) levels, including solvation effects within the polarizable continuum model (PCM). The following phenol derivatives were studied (their abbreviations are in parentheses): unsubstituted phenol (Phe), 2-methylphenol (2Me), 4-methylphenol (4Me), 3-nitrophenol ($3\mathrm{NO_2}$), 3-chlorophenol (3Cl), 2-chlorophenol (2Cl), 4-nitrophenol ($4\mathrm{NO_2}$), 2,3-dinitrophenol [$2,3(\mathrm{NO_2})_2$], 2,4-dinitrophenol [$2,4(\mathrm{NO_2})_2$], and 2,5-dinitrophenol [$2,5(\mathrm{NO_2})_2$]. In the next step, an attempt was done to correlate the calculated energetic parameters with the experimental values of acid dissociation constants, $\mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}}$, and anionic homoconjugation constants, $\log K_{\mathrm{AHA^-}}^{\mathrm{AN}}$ in acetonitrile (AN), as a representative of polar organic solvents.

Methods

All of the systems were optimized by the ab initio methods at the RHF (restricted Hartree−Fock) level using the GAMESS[13] program. The optimization was performed to a gradient of 0.0001 au/bohr (approximately 0.1 kcal $\mathrm{mol^{-1}}$ $\mathrm{Å^{-1}}$). In the calculations, the 6-31++G** basis set was used.

Equations 3 and 4 define the protonation (ΔE_{prot}) and anionic homoconjugation ($\Delta E_{\mathrm{AHA^-}}$) energies, respectively:

$$\Delta E_{\mathrm{prot}} = E_{\mathrm{HA}} - E_{\mathrm{A^-}} \tag{3}$$

$$\Delta E_{\mathrm{AHA^-}} = E_{\mathrm{AHA^-}} - (E_{\mathrm{HA}} + E_{\mathrm{A^-}}) \tag{4}$$

where $E_{\mathrm{AHA^-}}$ is the energy of a homocomplexed anion, E_{HA} is the energy of the proton donor, and $E_{\mathrm{A^-}}$ is the energy of the proton acceptor.

After optimization, translational, rotational, and vibrational energy contributions were calculated. Their values enabled one to check whether the stationary point found was a true minimum and to compute zero-point energy contributions (eqs 5 and 6).

The Gibbs free energies of protonation, ΔG_{prot}, and anionic homoconjugation, $\Delta G_{\mathrm{AHA^-}}$, were calculated from eqs 5 and 6, respectively:

$$\Delta G_{\mathrm{prot}} = \Delta E_{\mathrm{prot}} + \Delta E_{\mathrm{vib,prot}}{}^{\circ} + p\Delta V_{\mathrm{prot}} - T\Big[(S_{\mathrm{vib,HA}} + S_{\mathrm{rot,HA}}) - (S_{\mathrm{vib,A^-}} + S_{\mathrm{rot,A^-}}) - \frac{3}{2}R\Big] \tag{5}$$

$$\Delta G_{\mathrm{AHA^-}} = \Delta E_{\mathrm{AHA^-}} + \Delta E_{\mathrm{vib,AHA^-}}{}^{\circ} + p\Delta V_{\mathrm{AHA^-}} - T\Big[(S_{\mathrm{vib,AHA^-}} + S_{\mathrm{rot,AHA^-}}) - (S_{\mathrm{vib,HA}} + S_{\mathrm{rot,HA}} + S_{\mathrm{vib,A^-}} + S_{\mathrm{rot,A^-}}) - \frac{3}{2}R\Big] \tag{6}$$

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TABLE 1: Selected Geometric Parameters of Phenol and Its Derivatives,[a] Their Anionic Bases, and Homoconjugated Anions (Bond Lengths in Å, Angles in deg] Calculated in the 6-31++G Basis Set**

	base	acid			homoconjugated anion					
system	*d*(C−O)	*d*(C−O)	*d*(O−H)	∠(C−O−H)	*d*(O−O)	*d*(C−O)[b]	*d*(C−O)[c]	*d*(O−H)[c]	∠(C−O−H)[c]	∠(C[b]−O[b]−O[c]−C[c])
Phe	1.252	1.353	0.943	111.44	2.857	1.273	1.324	0.987	113.07	180.00
2Me	1.256	1.356	0.943	111.31	2.623	1.275	1.337	0.980	114.97	−153.20
4Me	1.254	1.355	0.943	111.35	2.585	1.276	1.326	0.987	112.83	−142.52
$3NO_2$	1.247	1.348	0.943	111.98	2.550	1.272	1.320	0.990	113.14	−145.28
3Cl	1.247	1.349	0.943	111.61	2.570	1.270	1.320	0.988	113.19	−148.17
2Cl	1.242	1.344	0.943	111.31	2.592	1.264	1.318	0.983	112.32	169.32
$4NO_2$	1.230	1.341	0.944	112.10	2.579	1.256	1.311	0.985	113.41	−144.28
$2,3(NO_2)_2$	1.222	1.331	0.944	110.52	2.566	1.259	1.313	0.985	112.33	−153.95
$2,5(NO_2)_2$	1.222	1.329	0.944	111.36	2.612	1.242	1.316	0.975	111.64	−104.19
$2,4(NO_2)_2$	1.215	1.322	0.945	111.46	2.609	1.235	1.305	0.976	113.58	−131.48

[a] Phenol derivative abbreviations: Phe, phenol; 2Me, 2-methylphenol; 4Me, 4-methylphenol; $3NO_2$, 3-nitrophenol; 3Cl, 3-chlorophenol; 2Cl, 2-chlorophenol; $4NO_2$, 4-nitrophenol; $2,3(NO_2)_2$, 2,3-dinitrophenol; $2,5(NO_2)_2$, 2,5-dinitrophenol; $2,4(NO_2)_2$, 2,4-dinitrophenol. [b] Proton acceptor. [c] Proton donor.

where $\Delta E_{\mathrm{vib,prot}}{}^{\circ}$ and $\Delta E_{\mathrm{vib,AHA^-}}{}^{\circ}$ are the differences between the zero-point vibrational energies of the products and those of the substrates, respectively, p is the pressure, and V is the volume of a system under the assumption that it satisfies the ideal gas equation-of-state; S_{rot} and S_{vib} are the rotational and vibrational entropies, respectively, and the term $^3/_2R$ refers to translational degrees of freedom of the system. A temperature of 298 K and a pressure of 1 atm were assumed in all calculations.

Subsequently, the perturbation theory was applied to further improve the calculated electronic energies of protonation and formation of the homocomplexed anions at the MP2 (Møller−Plesset) level.[14] The effect of dynamic correlation was calculated within a single iteration procedure for the structure optimized at the RHF level.[15] Such a procedure was used due to the complexity of the systems considered (large molecules and anions).

To estimate the solvation contributions to the protonation and homoconjugation energies, the polarizable continuum model (PCM) was applied. The PCM model[16] employs a van der Waals surface type cavity and parametrizes the cavity/dispersion contributions on the basis of the surface area. In this model, the free energy of a solvated system is described by two terms where the first term represents the solute Hamiltonian, which is modified by the electric field of the solvent. The second term includes both the solvent−solute stabilization energy and the reversible work needed to polarize the solvent. The second term is evaluated from the induced charges on the reaction field cavity surface. In this model, the dielectric constant of acetonitrile was assigned a value[17] of 35.94. Calculations were carried out for fixed geometries corresponding to the structures optimized in vacuo.

In systems consisting of at least two monomers (dimer or higher complex), the calculated interaction energy is decreased due to the fact that the basis set of the complex formed is artificially enlarged with respect to basis sets of the monomers. This causes an error called the basis set superposition error (BSSE). BSSE is estimated as the difference between the monomer energy values calculated in their basis sets and the energy values of monomers calculated in the basis set of the complex.[18] The calculations were performed by using the following general scheme (eqs 7) (they are analogous when calculating Gibbs free energies):

$$\Delta E_{\mathrm{BSSE}} = \Delta E_{\mathrm{complex}} - [E_{\mathrm{complex}}(\mathrm{A}) + E_{\mathrm{complex}}(\mathrm{B})] + (E_{\mathrm{A}} + E_{\mathrm{B}}) \quad (7)$$

where ΔE_{BSSE} denotes the interaction energy including BSSE correction, $\Delta E_{\mathrm{complex}}$ is the interaction energy value without consideration of BSSE (calculated as the difference between the energy of the complex and the sum of energies of the isolated subunits A and B), $E_{\mathrm{complex}}(\mathrm{A})$ and $E_{\mathrm{complex}}(\mathrm{B})$ are the energy values of complexes on the assumption that the orbitals of molecules A and B are the so-called “ghost” orbitals,[18] and E_{A} and E_{B} are the energy values of the A and B monomers, respectively.

Results and Discussion

In Table 1 are collected selected geometric parameters of the phenol and its substituted derivatives, their anionic forms (anionic bases), neutral forms (acids), and systems stabilized by the O···H···O bridges (homocomplexed anions). The C−O bond lengths of the anionic bases range from 1.215 to 1.256 Å, and for the conjugated acids (neutral species) they range from 1.322 to 1.356 Å. In the case of the homocomplexed anions, the lengths of the C−O bonds are longer by 0.02 Å as compared to those in the corresponding anionic bases and are shorter by 0.02 Å with respect to corresponding acids. The experimental value[20] of the C−O bond for phenol in the gas phase is 1.375 Å.

The lengths of the O−H bonds in neutral substituted phenols calculated in the 6-31++G** basis set are in the range 0.943−0.945 Å. The experimental[20] value obtained in the gas phase for the O−H distance in phenol is 0.957 Å, which is close to those collected in Table 1. The angles between the C−O−H atoms in the acids range from 110.52 to 112.10°, thus revealing sp^3 hybridization of the oxygen atom in this group. The experimental value[20] of this angle for phenol is 108.8°. Observed slight deviations of the calculated distances and angles from those characteristic for phenol are due to the presence of substituents in the ring.

The lengths of the O···O hydrogen bridges in the complexed anions vary between 2.550 and 2.623 Å, thus indicating strong hydrogen bonding in the homoconjugated anions. These values are similar to those previously calculated in the 6-31G* basis set for substituted pyridine *N*-oxides,[5] which range from 2.51 to 2.55 Å. This shows that in the homocomplexed anions of phenol and its derivatives, similar to the case of pyridine *N*-oxides, there is a strong symmetric hydrogen bonding. The lengths of the hydrogen bridges depend on the type of substituents in the phenol ring. They are longer for 2Me, 2Cl, $2,5(NO_2)_2$, and $2,4(NO_2)_2$ derivatives than for unsubstituted phenol. This phenomenon can be explained in terms of the so-called ortho effect. In all cases, the C−O bonds in the homocomplexed anions are longer in proton acceptors by ca.

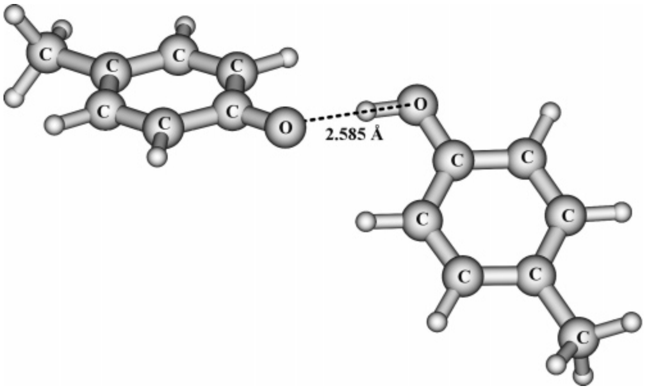

Figure 1. An example structure of the anionic homocomplex formed by the 4-methylphenol (4Me) and stabilized by hydrogen bonding. The dashed line denotes hydrogen bonding.

TABLE 2: Calculated Energies, ΔE_{prot}(RHF), and Gibbs Free Energies, ΔG_{prot}(RHF), of Protonation at the RHF Level, as well as MP2, ΔE_{prot}(MP2), and PCM, ΔG_{prot}(PCM), Protonation Energies and Gibbs Free Energies, Respectively, for Phenol Derivatives (kcal/mol)[a]

phenol derivatives[b]	ΔE_{prot}(RHF)	ΔG_{prot}(RHF)	ΔE_{prot}(MP2)	ΔG_{prot}(PCM)	[c]$\text{p}K_a^{\text{AN}}$
Phe	−354.15	−354.45	−356.07	−56.53	25.74[d]
2Me	−355.16	−356.29	−356.90	−59.77	26.25
4Me	−356.16	−356.28	−357.26	−58.46	26.35
3NO$_2$	−339.30	−339.36	−340.27	−52.49	23.93
3Cl	−346.06	−346.39	−348.33	−53.91	23.99
2Cl	−345.36	−345.64	−348.13	−51.71	23.08
4NO$_2$	−329.61	−329.99	−333.69	−45.60	21.39
2,3(NO$_2$)$_2$	−318.97	−321.02	−325.29	−39.35	17.87
2,5(NO$_2$)$_2$	−321.78	−319.83	−328.09	−42.42	18.73
2,4(NO$_2$)$_2$	−311.28	−311.45	−317.81	−34.86	16.33

[a] All calculations were carried out using the 6-31++G** basis set. Experimental $\text{p}K_a^{\text{AN}}$ values in acetonitrile included for comparison [ref 11]. [b] Phenol derivative abbreviations: Phe, phenol; 2Me, 2-methylphenol; 4Me, 4-methylphenol; 3NO$_2$, 3-nitrophenol; 3Cl, 3-chlorophenol; 2Cl, 2-chlorophenol; 4NO$_2$, 4-nitrophenol; 2,3(NO$_2$)$_2$, 2,3-dinitrophenol; 2,5(NO$_2$)$_2$, 2,5-dinitrophenol; 2,4(NO$_2$)$_2$, 2,4-dinitrophenol. [c] Data from ref 11. [d] Experimental $\text{p}K_a^{\text{AN}}$ value for phenol in acetonitrile was calculated from the following equation: $\text{p}K_a^{\text{AN}} = 1.55\text{p}K_a^{\text{W}} + 10.27$, which was taken from ref 11, where $\text{p}K_a^{\text{W}}$ was taken as 9.98 from ref 19.

0.02 Å relative to those in the molecules of the corresponding phenol derivatives. This is indicative of a strong affinity of the proton toward the oxygen of the C−O group. In the proton donors, the lengths of the C−O bonds are only slightly shorter (by approximately 0.02 Å). Again, in the case of homoconjugated anions, the O−H bonds are significantly longer than those in the corresponding molecular acids conjugated with anionic bases. In each system, the difference oscillates around 0.04 Å. On this basis, it can be anticipated that there is a possibility of free proton transfer (or through a very low-energy barrier) from the proton donor to proton acceptor as it was observed in the case of the homocomplexed pyridine *N*-oxide cation.[5] Moreover, the angle between the C−O−H atoms in the molecules of the proton donors undergoes deformation. In the homocomplexed anions, it changes between 111.64 and 114.97°, whereas the experimental value[20] of that angle in phenol is 108.8°. Examination of dihedral angles between the C−O−O−C atoms, where the first C−O atoms belong to proton acceptors and the next two belong to proton donors, shows that the homocomplexed anions are not coplanar; that is, the proton donor and proton acceptor do not lie in one plane (Figure 1). These angles range from 104.19 to 180.00°. It can also be seen that the more the angle deviates from linearity (180 deg), the longer is the O···O bridge and the weaker is the hydrogen bonding. The deviation from the linearity depends on the type of substituent in the phenol ring. The ideal planar position can be observed for the homocomplexed system formed by unsubstituted phenol. Accordingly, the formation energies of the homocomplexed cations formed by the substituted 4-nitropyridine *N*-oxides are likely to decline in the same direction.[7]

Table 2 lists protonation energies, ΔE_{prot}, determined at the RHF and MP2 levels and Gibbs free energies, ΔG_{prot}, determined at the RHF level, as well as within the PCM model accounting for interactions with the solvent. For the sake of comparison, $\text{p}K_a^{\text{AN}}$ constants determined by potentiometric titration in acetonitrile[11] representing polar nonaqueous solvents are also included in this table. The phenol and its methyl and chloro derivatives display higher absolute values of the protonation energies than the nitro derivatives. This means that the anions of phenol and its methyl derivatives are stronger bases than the mono and dinitro and, consequently, the conjugate phenols should have higher pK_a values. Their increased basicity can be explained by the fact that the methyl group has electron-donor tendency, which increases electron density on the oxygen atom in OH group. Consequently, the probability of proton dissociation from the OH group is lower. Comparison of the calculated and experimental $\text{p}K_a^{\text{AN}}$ values seems to support this hypothesis. The experimental $\text{p}K_a^{\text{AN}}$ values for phenol and its methyl and chloro derivatives are about 10 units of magnitude higher than those for nitro derivatives. The protonation energies of the nitro derivatives obtained by the MP2 method range between −317.81 and −340.27 kcal mol^{-1}, whereas those for the methyl and chloro derivatives range from −348.13 to −357.26 kcal mol^{-1}, thus being 8−39 kcal mol^{-1} higher (taking into account their absolute values). The $\text{p}K_a^{\text{AN}}$ values show a similar tendency. For the 2-methyl and 4-methyl phenol derivatives, the experimental pK_a values determined in acetonitrile are 26.25 and 26.35 for 2-methyl and 4-methyl, respectively, whereas for the dinitro compounds they are about 9 pK_a units lower.

Further, a closer look at Table 2 shows that both the calculated and the experimental values change in the same direction. On this basis, an attempt was made to establish linear correlations between the $\text{p}K_a^{\text{AN}}$ values and the calculated ΔE_{prot}(RHF), ΔG_{prot}(RHF), and ΔE_{prot}(MP2) values in the gas phase, on one hand, and the ΔG_{prot}(PCM) values accounting for solvation effects, on the other hand. The correlations can be represented as the following linear functions (where R is the correlation coefficient):

$$\text{p}K_a^{\text{AN}} = -0.22(0.01)\Delta E_{\text{prot}}(\text{RHF}) - 51.47(4.47) \qquad R = -0.986 \quad (8)$$

$$\text{p}K_a^{\text{AN}} = -0.22(0.01)\Delta G_{\text{prot}}(\text{RHF}) - 50.70(4.82) \qquad R = -0.983 \quad (9)$$

$$\text{p}K_a^{\text{AN}} = -0.25(0.02)\Delta E_{\text{prot}}(\text{MP2}) - 61.91(6.66) \qquad R = -0.976 \quad (10)$$

$$\text{p}K_a^{\text{AN}} = -0.42(0.02)\Delta G_{\text{prot}}(\text{PCM}) + 1.57(0.89) \qquad R = -0.994 \quad (11)$$

An example plot is shown in Figure 2, where $\text{p}K_a^{\text{AN}}$ is plotted against ΔG_{prot}(PCM). The relatively high R-values reveal a strong correlation between the acidities of the phenol and its derivatives studied in vacuo and those determined in solution. Similar correlations were established previously for monosub-

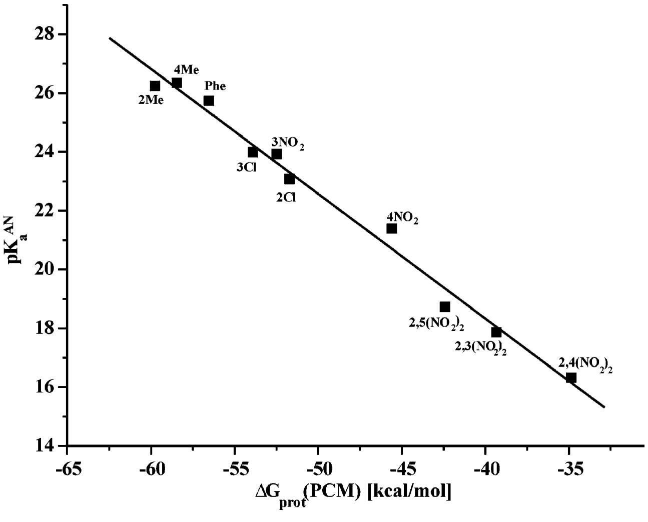

Figure 2. Plot of pK_a^{AN} against ΔG_{prot}(PCM) for phenol and its derivatives studied. The abbreviations for the systems are given in the graph.

stituted pyridine *N*-oxides[5,7] and pyridine derivatives.[6] It should be noted that the quality of these correlations does not increase significantly upon going from the RHF to the MP2 level. This means that even the relatively cheap ab initio calculations accomplished at the RHF level enable prediction of the sequence of acidity constants of the phenol derivatives in polar organic solvents. The best correlation coefficient was determined after consideration of the solvation effects within the PCM model. The correlation coefficient was $R = 0.994$ (eq 11).

The energies and Gibbs free energies of formation of the homocomplexed anions calculated at both levels, as well as after considering solvation effects within the PCM model in acetonitrile, are collected in Table 3. In the table, there are also values calculated at the RHF level after considering the base superposition set error (BSSE). The strongest impact of BSSE on energetic parameters is seen for the disubstituted compounds. For the sake of comparison, also included are logarithms of the anionic homoconjugation constant values of phenol and its derivatives (log $K_{AHA^-}^{AN}$) determined in acetonitrile[11,21] solutions. Similarly to the case of the protonation reactions, an attempt was made to correlate energetic parameters of the anionic homoconjugation with experimental anionic homoconjugation constants in acetonitrile. After consideration of all of the derivatives, the correlation coefficients were very low, ranging between 0.1 and 0.4. Rejection of three or more points from the correlation improved the coefficients significantly, but from the statistical point of view it is forbidden and such results are doubtful. It can thus be concluded that there are not even weak linear correlations for the phenol and substituted phenol derivatives between the calculated energetic parameters of the anionic homoconjugation calculated in the gas phase, or after the inclusion solvent effect and experimentally derived constants of this equilibrium determined in acetonitrile.

Conclusions

Ab initio calculations at the RHF and MP2 levels, and with the PCM model, utilizing the Gaussian 6-31++G** basis set, for phenol and nine substituted derivative systems enabled us to draw the following conclusions.

Inexpensive ab initio calculations at the RHF, MP2, and PCM levels and by using the 6-31++G** basis set enable the prediction of the sequence of acid dissociation constant values of phenol derivatives in polar organic solvents. The calculated protonation energies, ΔE_{prot}, and Gibbs free energies, ΔG_{prot}, of the substituted phenols studied correlate well with the acid dissociation constants in acetonitrile solutions (expressed as pK_a^{AN} values).

TABLE 3: Calculated Energies, ΔE_{AHA^-}(RHF), and Gibbs Free Energies, ΔG_{AHA^-} (RHF), of Protonation at the RHF Level, as well as MP2, ΔE_{AHA^-}(MP2), and PCM, ΔG_{AHA^-} (PCM), Homoconjugation Energies and Gibbs Free Energies, Respectively, for Phenol and Its Derivatives (kcal/mol)[a]

phenol derivatives[b]	ΔE_{AHA^-}(RHF) (BSSE)	ΔG_{AHA^-}(RHF) (BSSE)	ΔE_{AHA^-} (MP2)	ΔG_{AHA^-} (PCM)	[c]log $K_{AHA^-}^{AN}$
Phe	−22.10 (−21.77)	−11.48 (−11.11)	−28.79	−6.80	4.80[d]
2Me	−18.27 (−18.27)	−7.37 (−6.44)	−26.94	−3.91	3.42
4Me	−22.07 (−21.46)	−10.07 (−9.39)	−28.71	−6.63	3.02
$3NO_2$	−25.39 (−24.88)	−13.60 (−13.17)	−32.57	−7.58	4.33
3Cl	−23.65 (−23.11)	−10.24 (−10.18)	−30.56	−6.58	3.27
2Cl	−23.28 (−23.14)	−13.94 (−13.80)	−30.87	−6.32	2.88
$4NO_2$	−24.77 (−24.77)	−12.94 (−12.93)	−31.35	−7.02	3.61
$2,3(NO_2)_2$	−23.09 (−19.61)	−9.76 (−7.57)	−39.36	−12.84	4.12
$2,5(NO_2)_2$	−27.60 (−23.97)	−13.96 (−10.31)	−37.01	−10.20	2.65
$2,4(NO_2)_2$	−22.57 (−22.55)	−11.47 (−11.42)	−32.99	−4.47	2.26

[a] All calculations were carried out using the 6-31++G** basis set. Experimental log $K_{AHA^-}^{AN}$ values in acetonitrile were included for comparison [refs 11 and 21]. In parentheses were included BSSE energies. [b] Phenol derivative abbreviations: Phe, phenol; 2Me, 2-methylphenol; 4Me, 4-methylphenol; $3NO_2$, 3-nitrophenol; 3Cl, 3-chlorophenol; 2Cl, 2-chlorophenol; $4NO_2$, 4-nitrophenol; $2,3(NO_2)_2$, 2,3-dinitrophenol; $2,5(NO_2)_2$, 2,5-dinitrophenol; $2,4(NO_2)_2$, 2,4-dinitrophenol. [c] Data from ref 11. [d] Experimental log $K_{AHA^-}^{AN}$ value for phenol in acetonitrile was calculated from the following equation: log $K_{AHA^-}^{AN} = 0.282pK_a^{AN} - 2.46$, which was taken from ref 11, where pK_a^{AN} was taken from Table 2.

The introduction of solvation effects in the PCM model improves the correlation between the calculated protonation energies (Gibbs free energies) and the experimental pK_a^{AN} values of substituted phenols in acetonitrile.

The variation of the anionic homoconjugation constants on systems formed by phenol and its derivatives and conjugated bases in polar nonaqueous solvent acetonitrile can be predicted on the basis of energies and Gibbs free energies calculated by the ab initio methods, assuming that the BSSE effect is taken into account.

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