Hydrogen Bonding of Phenols or Their Radical Cations with Water or Ammonia: Substituent Effects and the Influence on Phenol Oxidation

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We did UB3LYP/6-31++g** and ROMP2/6-311++g** calculations on the hydrogen bonding of para-substituted phenols and their radical cations with water and ammonia. It was found that the magnitudes of the proton affinities increase in the order water (165 kcal/mol) < ammonia (204 kcal/mol) ≈ phenoxyl radicals (193−235 kcal/mol) < phenolate anions (321−352 kcal/mol). The slopes of the proton affinities against the substituent σ_p constants are about 22 and 15 kcal/mol for phenoxyl radicals and phenolate anions. It was also found that the slopes of the binding energies against the substituent σ_p constants decrease in the order phenol−water complex (1.1 kcal/mol) < phenol−ammonia complex (1.4 kcal/mol) < phenol radical cation−water complex (4.1 kcal/mol) < phenol radical cation−ammonia complex (9.3 kcal/mol). The structure of the substituted phenol radical cation−ammonia complex was found to rely on the proton affinity of the corresponding phenoxyl radical. When the proton affinity is larger than 214 kcal/mol, the non-proton-transferred form is the only minimum on the potential energy surface. When the proton affinity is smaller than 210 kcal/mol, the proton-transferred form is the only minimum. The only complex for which both the proton-transferred and non-proton-transferred forms are minima was found for *p*-hydroxylphenol radical cation. On the other hand, all the phenol radical cation complexes with water have the non-proton-transferred form as the only minimum on the potential surface. Hydrogen bonding to ammonia was found to lower the adiabatic oxidation potentials of phenols by 0.5−1.2 eV. Hydrogen bonding to water was found to lower the adiabatic oxidation potentials of phenols by 0.4−0.6 eV. In general, a phenol substituted with a more electron-withdrawing group shows larger reduction in the adiabatic oxidation potential when complexed to water or ammonia.

1. Introduction

Phenols are good electron donors because of their relatively low ionization energies. As a result, phenols are widely used as antioxidants to inhibit the oxidative degradation of organic materials in many biological aerobic organisms and commercial products.[1] Usually, the product from phenol oxidation is either phenol radical cation through a direct single electron transfer or phenoxyl radical via a proton-coupled electron transfer.[2] Both pathways are currently of great interest in chemistry. Therefore, phenols are also widely used as model systems in the study of photoinduced electron transfer and proton-coupled electron transfer.[3]

In addition to material science and physical organic chemistry, phenol oxidation is also important in biochemistry. In fact, in the form of tyrosine/tyrosyl radical transformation the phenol oxidation plays crucial roles in many biological systems including photosynthetic system, cytochrome *c* oxidase, human catalase, and ribonucleotide reductase.[4] Interestingly, in different enzymes the role of phenol oxidation could be completely different. Such a variation can only be caused by the different chemical environments that different phenol/phenoxyl radical pairs are surrounded by. Detailed studies into these subtle environmental effects are of considerable interest at the present stage.[5]

A bottom-up approach to study the environmental effects on phenol oxidation is to construct the supramolecular systems where phenol or phenoxyl radical cation is allowed to interact with other small molecules. Both experimental and theoretical methods have been used in such studies. For example, in 1994 Schlag et al. studied the zero-kinetic-energy photoelectron spectroscopy of the phenol−water radical cation,[6] which was followed by a theoretical study using ROHF and ROMP2 methods with 3-21g* and 6-31g* basis sets.[7] It was found that the most stable structure for the complex involved a linear hydrogen bond between the proton of the OH group of phenol radical cation and the oxygen of water. The interaction energy of the noncovalent radical cation complex was found to be considerably larger than the usual van der Waals molecules.

In a later study by Mons et al., the complexes of phenol radical cation with solvent molecules including water, methanol, and dimethyl ether were studied with the two-color two-photo resonant ionization laser technique.[8] Compared with the interaction energies of the neutral complexes of phenol with water, methanol, and dimethyl ether, which are about 6 kcal/mol, the interaction energies of the radical cation complexes were found through experiments to be about 20 kcal/mol. These values could also be reproduced reasonably well using theoretical methods such as MP2/6-31g**.

Another interesting study was performed by Osamura et al.[9] They used HF, MP2, and B3LYP methods with DZP basis set to calculate the hydrogen-bonded clusters between phenol radical

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cation and an increasing number ($n = 1-4$) of water molecules. It was found that the position of the proton of phenol radical cation depended on the number of water molecules in the cluster; i.e., in the $n = 1$ and 2 cluster ions there was no proton transfer whereas in the cluster ions $n \geq 3$ proton transfer occurred simultaneously. Therefore, the size of water cluster determines whether the electron transfer is coupled with a proton transfer. This interesting finding was in agreement with the experimental observations.[10]

In comparison to the above agreement, there is much controversy between the experimental and theoretical results on the phenol−ammonia radical cation complex. Although from both studies it was concluded that the proton-transferred $C_6H_5O^{\bullet-}NH_4^+$ complex was the most stable structure, experimental studies suggested that there was a larger energy barrier (∼1 eV) for the proton transfer from $C_6H_5OH\bullet^{+-}NH_3$ to $C_6H_5O^{\bullet-}NH_4^+$.[11] This energy barrier, however, could not be reproduced by the theoretical studies either at UHF/6-31+g* level by Scheiner et al.[12] or at B3LYP/D95++** level by Bertran et al.[13] Instead, according to theories only the proton-transferred $C_6H_5O\bullet-NH_4^+$ structure was found to be the real minimum on the potential surface of the radical cation complex. As a result, it was concluded that the corresponding proton transfer was barrierless. It should be mentioned that in a very recent experimental study using mass-analyzed threshold ionization method, it was confirmed that there should be no significant barrier to proton transfer on the potential surface of $C_6H_5O\bullet-NH_4^+$.[14]

In addition to proton transfer, another important consequence of hydrogen bonding to phenol radical cation is the decrease of the ionization potential. In particular, in close relevance to the tyrosine/tyrosyl radical redox found in photosystem II, theoretical calculations using B3LYP method with various basis sets showed that hydrogen bonding to imidazole could significantly lower the adiabatic ionization potential of phenol by ca. 1 eV.[15] Such a regulation effect was proposed to make possible oxidation of tyrosine by a relatively weak electron acceptor. Besides, as the hydrogen bonding to imidazole was found to be able to switch on a proton-coupled electron transfer, its regulation effect was also believed to be important in making the biological phenol oxidation fast and efficient.

We became interested in phenol oxidation when we initiated our studies on the biomimetic electron-transfer reactions.[16] Phenols would be interesting substrates for our research because of their nice electron donor properties as well as their good biological relevance. It would be highly desirable to construct supramolecular systems containing phenol moiety as the electron donor, whose redox properties could then be effectively regulated via certain noncovalent interactions. Clearly, to better control the system we need to get some insights into the relationships between the noncovalent interactions and redox properties of phenol before doing experiments. As a result, we performed systematic studies on the effects of hydrogen bonding on phenol oxidation.

Our first series of results dealt with the effects of hydrogen bonding to various amines on phenol oxidation.[17] We found good relationship between the amine basicity and the oxidation potentials, product structures, and shapes of potential surfaces. These results would be of help when one tries to introduce a partner molecule to regulate the phenol oxidation. In the present study we were interested in the phenol portion itself, i.e., the substituent effects on phenol oxidation. In detail, we studied the redox properties of various substituted phenols, phenol−water complexes, and phenol−ammonia complexes, including the structures, energies, shapes of potential surfaces, and structure−activity relationships. It should be mentioned that studies closely related to the present one can also be found in the literature, for example, in a recent one on phenol derivative−ammonia complexes.[18] Thus, an additional goal for the present study is to double check the literature results.

2. Method

All the calculations were performed using Gaussian 98.[19] All the optimizations were conducted using the UB3LYP/6-31++g** method. Every optimized structure was also confirmed by the UB3LYP/6-31++g** frequency calculation to be real minimum without any imaginary frequency. The zero point energy of every species was also obtained at UB3LYP/6-31++g** level (unscaled). It should be mentioned that the DFT, in particular UB3LYP, method is the fairly good for the geometry optimization at a reasonable CPU cost. In fact, recent studies even showed that the accuracy of B3LYP in the geometry optimization and frequency calculations is roughly comparable to, or even better than, the CCSD method.[20] By contrast, Hartree−Fock and MP2 methods, either restricted open-shell or unrestricted, work in a much less reliable way for the geometry optimization of radicals.[20]

The single point energy of every species was calculated at both UB3LYP/6-31++g** and ROMP2/6-311++g** levels, both corrected with the zero point energy obtained at UB3LYP/6-31++g** level (unscaled). Here, use of ROMP2 in addition to UB3LYP method was based on the Radom's finding that ROMP2 calculations usually could predict the energies of radicals better than UB3LYP method.[21] Use of the two methods based on quite different theories would also help us confirm the reliability of the calculation results.

The hydrogen bonding energy of the phenol and phenol radical cation complexes were calculated from the difference between the total energy of the complex and the sum of the total energies of the corresponding monomers at ROMP2/6-311++g** and UB3LYP/6-31++g** levels. This interaction energy was corrected with the UB3LYP/6-31++g** zero point energies (unscaled) as well as the basis set superposition error (BSSE) estimated with the full counterpoise procedure at the ROMP2/6-311++g** or UB3LYP/6-31++g** level, respectively.[22]

The proton affinity of a species A was calculated as the enthalpy change of the following chemical reaction at 298 K in gas phase.

$$A + H^+ \rightarrow AH^+ \qquad (1)$$

ROMP2/6-311++g**//UB3LYP/6-31++g** and UB3LYP/6-31++g**//U B3LYP/6-31++g** methods were used. The zero point energies, finite temperature (0−298 K) correction, and the pressure−volume work term were all taken into account in the calculations of proton affinities, as enthalpies at 298 K were evaluated using

$$H_{298} = E + \text{ZPE} + \Delta H_{298-0} + RT \qquad (2)$$

The enthalpy of the proton is (5/2)RT.

The adiabatic ionization potential in the gas phase was calculated as the energy difference between a ground-state molecule (or complex) and its radical cation. The energy was converted to its corresponding value at 298 K by the zero point energy finite temperature (0−298 K) corrections.

3. Results and Discussion

3.1. Substituent Effects on the Oxidation of Free Phenols. Before we study the hydrogen-bonded complexes, we would

TABLE 1: Proton Affinities of Substituted Phenolate Anions and Phenoxyl Radicals (kcal/mol)

		phenolate anion			phenoxyl radical	
substituent	σ_p	(U)B3LYP/6-31++g**// (U)B3LYP/6-31++g**	ROMP2/6-311++g**// (U)B3LYP/6-31++g**	expt[a] (600 K)	(U)B3LYP/6-31++g**// (U)B3LYP/6-31++g**	ROMP2/6-311++g**// (U)B3LYP/6-31++g**
$-N(CH_3)_2$	−0.83	−347.5	−347.3		−234.8	−233.7
$-NH_2$	−0.66	−350.7	−351.5		−226.8	−223.4
−OH	−0.37	−348.8	−349.9	−343.8	−215.9	−211.7
$-OCH_3$	−0.27	−349.0	−350.2	−347.6	−220.1	−215.7
$-CH_3$	−0.17	−348.1	−349.4	−348.2	−213.0	−207.1
$-CH{=}CH_2$	−0.04	−339.7	−342.5		−214.2	−210.2
−H	0.00	−346.8	−348.3	−346.9	−206.5	−207.4
$-SCH_3$	0.00	−339.9	−342.2		−224.2	−221.3
−F	0.06	−343.7	−345.5	−344.3	−204.5	−206.4
−SH	0.15	−339.6	−342.2		−218.0	−214.4
−CCH	0.23	−337.3	−340.4		−213.2	−207.6
−Cl	0.23	−340.3	−342.8	−340.3	−207.2	−202.2
−COOH	0.45	−331.7	−335.1		−202.2	−196.4
$-COCH_3$	0.50	−332.0	−335.4		−205.3	−198.3
$-CF_3$	0.54	−333.1	−335.4		−197.7	−200.5
−CN	0.66	−328.5	−331.7	−329.2	−197.9	−191.9
$-NO_2$	0.78	−321.9	−327.9		−193.0	−198.3

[a] Taken from: Voets, R.; Francois, J.-P.; Martin, J. M. L.; Mullens, J.; Yperman, J.; van Poucke, L. C. *J. Comput. Chem.* **1990**, *11*, 269.

TABLE 2: Adiabatic Ionization Potentials of Substituted Phenols in the Gas Phase (eV)

substituent	(U)B3LYP/6-31++g**// (U)B3LYP/6-31++g**	ROMP2/6-311++g**// (U)B3LYP/6-31++g**
$-N(CH_3)_2$	6.63	6.67
$-NH_2$	7.02	7.16
−OH	7.64	7.76
$-OCH_3$	7.45	7.56
$-CH_3$	7.90	8.07
$-CHCH_2$	7.61	7.78
−H	8.27	8.41
$-SCH_3$	7.31	7.42
−F	8.29	8.36
−SH	7.62	7.73
−CCH	7.90	8.12
−Cl	8.20	8.29
−COOH	8.57	8.68
$-COCH_3$	8.41	8.60
$-CF_3$	8.78	8.91
−CN	8.74	8.88
$-NO_2$	9.05	9.02

like to know the properties of isolated substituted phenols and phenol radicals including proton affinities and oxidation potentials. The results are listed in Tables 1 and 2.

From Table 1, it can be seen that the phenolate anions have large proton affinities ranging from about 320 to 350 kcal/mol. The differences between the UB3LYP/6-31++g** and ROMP2/6-311++g** results are small, and are usually less than 1−2 kcal/mol. Also, except for the hydroxyl substitution, the agreement between the theoretical and experimental proton affinities (at 600 K) is within 2 kcal/mol, which is as large as the temperature correction for the proton enthalpy [$(5/2)R\Delta T = 1.5$ kcal/mol]. As a result, we can conclude that the calculated phenolate proton affinities are fairly accurate.

In comparison, the agreement between the UB3LYP/6-31++g** and ROMP2/6-311++g** proton affinities of phenoxyl radicals is less satisfactory. For most of the substituents, the difference between the two theoretical results is about 4−5 kcal/mol. We do not know which method is better as there are few experimental data about phenoxyl radicals. Nevertheless, the experimental proton affinity of phenol radical was measured recently to be 208.7 kcal/mol,[14] which is compared to our values, 206.5 kcal/mol at UB3LYP/6-31++g** level and 207.4 kcal/mol at ROMP2/6-311++g** level.

At this point, it should be mentioned that the proton affinity of water is calculated to be 163.6 kcal/mol at UB3LYP/6-31++g** level and 164.5 kcal/mol at ROMP2/6-311++g** level, compared to the experimental value of 165.1 kcal/mol. The proton affinity of ammonia is calculated to be 203.2 kcal/mol at UB3LYP/6-31++g** level and 203.9 kcal/mol at ROMP2/6-311++g** level, compared to the experimental value of 204.1 kcal/mol.[23] Therefore, the magnitudes of proton affinity increase in the order water < ammonia ≈ phenol radical < phenolate anion.

According to Table 1, the substituents affect the proton affinities of phenol and phenolate anion in a systematic way. An electron-donating substituent lowers the proton affinity, whereas an electron-withdrawing group increases it. Mathematically, we can plot the proton affinities (PA) against the substituent σ_p constants (eqs 3−6).

$$\mathrm{PA(phenolate,UB3LYP)} = -341.2 + 16.8\sigma_p (r = 0.91) \quad (3)$$

$$\mathrm{PA(phenolate,ROMP2)} = -343.3 + 14.1\sigma_p (r = 0.90) \quad (4)$$

$$\mathrm{PA(radical,UB3LYP)} = -213.4 + 22.7\sigma_p (r = 0.89) \quad (5)$$

$$\mathrm{PA(radical,ROMP2)} = -210.4 + 21.6\sigma_p (r = 0.89) \quad (6)$$

It should be mentioned that using the experimental data, we have

$$\mathrm{PA(phenolate,expt)} = -343.2 + 16.6\sigma_p (r = 0.87) \quad (7)$$

Therefore, the calculation results agree well with the experimental ones in the regression slope as well as intercept. It should be mentioned that these Hammett regression results are important, because using them one could easily predict or check the proton affinity of any para-substituted phenol or phenoxyl radical. The positive slopes of the above regressions indicate that an electron-withdrawing group lowers the absolute proton affinity, whereas an electron-donating group increases the absolute proton affinity.In Table 2 are summarize the gas-phase adiabatic ionization potentials of phenols. From this table it can be seen that the difference between the UB3LYP/6-31++g** and ROMP2/6-311++g** results is usually less than 0.2 eV. For phenol the UB3LYP/6-31++g** calculation predicts the ionization potential to be 8.27 eV, whereas the ROMP2/6-311++g** method gives a value of 8.41 eV. These results should be compared with the UB3LYP/6-311++g** value, 8.35

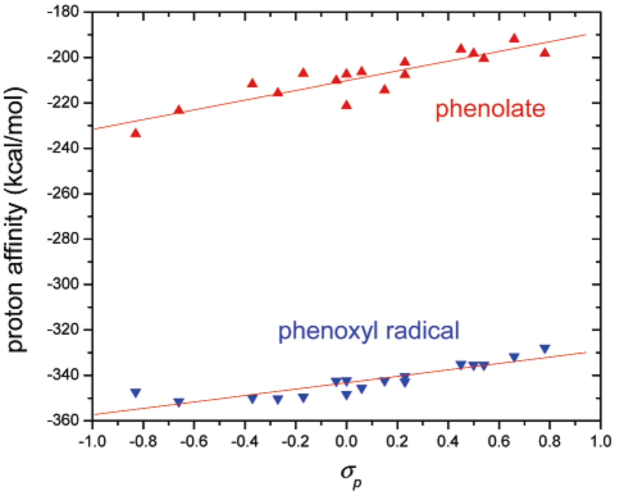

Figure 1. Correlation between substituent σ_p constants and calculated proton affinities of phenolate anions and phenoxyl radicals (ROMP2/6-311++g**).

eV, and the experimental value, 8.49 eV.[24] For hydroquinone UB3LYP/6-31++g** and ROMP2/6-311++g** predict the ionization potential to be 7.64 and 7.76 eV. The corresponding experimental value was reported to be 7.94 eV.[25]

The substituent effects on the adiabatic ionization potential (IP) can also be revealed by the Hammett regressions (eqs 8 and 9).

$$\mathrm{IP(UB3LYP)} = 7.9 + 1.4\sigma_p (r = 0.91) \tag{8}$$

$$\mathrm{IP(ROMP2)} = 8.0 + 1.4\sigma_p (r = 0.92) \tag{9}$$

Using these equations, one is able to estimate the ionization potential of any para-substituted phenol.

3.2. Hydrogen Bonding of Neutral Substituted Phenols with Water and Ammonia. Hydrogen bonding between phenol and water (or ammonia) has been studied with various experimental and theoretical methods. For the phenol−water complex, successful measurement of the binding energy was done only recently.[8,26] The value was found to be 5.48−5.60 kcal/mol. In comparison, our theoretical value for the same interaction is 4.49 kcal/mol at UB3LYP/6-31++g** level and 4.16 kcal/mol at ROMP2/6-311++g** level. A previous theoretical value at MP2/6-311++g** level (using HF-optimized geometries) was 4.35 kcal/mol.[27] Recently van Mourik also reported a value of 5.04 kcal/mol at MP2/ESPB level.[28] The difference between the experimental and theoretical results may be caused by an overestimated BSSE correction, which has been known to be a problem for the full counterpoise procedure.[29] In addition, neglecting the anharmonicity contributions to the vibration may lead to a too-large zero point energy correction. However, as the ZPE correction for the interaction energy between phenol and water is calculated to be 1.74 kcal/mol, it is not appropriate to completely omit it.

We did not find the experimental binding energy for the phenol−ammonia complex. Nevertheless, theoretical results for this complex are abundant in the literature. At BLYP/6-31g-(d,p) level, the binding energy of the phenol−ammonia complex was calculated to be 7.45 kcal/mol without ZPE correction.[18] This energy was also predicted to be about 8.1−9.5 kcal/mol without ZPE correction at B3LYP and MP2 levels with various basis sets including D95*, D95++*, and DZP.[9,13] Our calculation on the same complex gives a binding energy of 8.40 and 7.82 kcal/mol without ZPE correction at UB3LYP/6-31++g** and ROMP2/6-311++G** levels. However, as the ZPE correction is calculated to be 1.77 kcal/mol, our final binding energy for phenol−ammonia complex is 6.63 or 6.05 kcal/mol at UB3LYP/6-31++g** or ROMP2/6-311++G** level. Compared to the phenol−water case aforementioned (5.6 kcal/mol from experiment vs 4.5 kcal/mol from UB3LYP theory), the real phenol−ammonia binding energy might be about 7.7 kcal/mol. Interestingly, the binding energy between 1-naphthol and ammonia was experimentally measured to be 7.66 kcal/mol.[30]

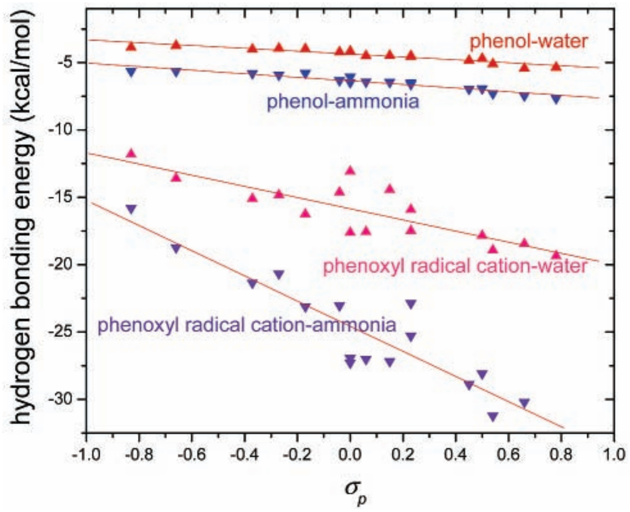

Figure 2. Correlation between substituent σ_p constants and calculated hydrogen bonding interaction energies (ROMP2/6-311++g**).

Although the calculated hydrogen bonding interaction energies are smaller than the experimental ones, we believe that the calculated substituent effects on the hydrogen bonding are fairly accurate. The reason for this assumption is that the ZPE corrections for all the water complexes vary from 1.74 to 1.83 kcal/mol, and for all the ammonia complexes they vary from 1.77 to 1.90 kcal/mol. Therefore, the small difference in the ZPE correction (~0.1 kcal/mol) should not significantly affect the slopes of the following regressions for the hydrogen bonding interaction strength (D):

$$D_{\mathrm{phenol-ammonia}}\mathrm{(UB3LYP)} = -7.0 - 1.9\sigma_p (r = 0.97) \tag{10}$$

$$D_{\mathrm{phenol-ammonia}}\mathrm{(ROMP2)} = -6.4 - 1.3\sigma_p (r = 0.95) \tag{11}$$

$$D_{\mathrm{phenol-water}}\mathrm{(UB3LYP)} = -4.8 - 1.4\sigma_p (r = 0.96) \tag{12}$$

$$D_{\mathrm{phenol-water}}\mathrm{(ROMP2)} = -4.4 - 1.1\sigma_p (r = 0.94) \tag{13}$$

Comparing the UB3LYP or ROMP2 slopes, we can conclude that the substituent effects on the phenol−ammonia binding energies are slightly larger than the phenol−water ones.

3.3. Hydrogen Bonding of Phenol Radical Cations with Ammonia and Water. The hydrogen bonding between phenol radical cation and ammonia is a little complicated as the complex structure could either be $X{-}C_6H_4{-}O{-}H^{\bullet+}\cdots NH_3$ or $X{-}C_6H_4{-}O^{\bullet}\cdots NH_4^+$. The former one is a non-proton-transferred complex. The latter is a proton-transferred complex.

The early experimental studies on the phenol radical cation−ammonia complex suggested that both the non-proton-transferred and proton-transferred forms were real minima on the potential energy surface separated by a substantial barrier.[11,31] However, recent ab initio calculations at various levels[12,13,15] and experimental study using mass-analyzed threshold ionization technique[14] all suggested that the proton-transferred complex

TABLE 3: Hydrogen Bonding Interaction Energies between the Neutral Phenol and Water and Ammonia (kcal/mol)

substituent	ammonia		water	
	(U)B3LYP/6-31++g**// (U)B3LYP/6-31++g**	ROMP2/6-311++g**// (U)B3LYP/6-31++g**	(U)B3LYP/6-31++g**// (U)B3LYP/6-31++g**	ROMP2/6-311++g**// (U)B3LYP/6-31++g**
$-N(CH_3)_2$	−5.85	−5.64	−3.88	−3.87
$-NH_2$	−5.97	−5.64	−4.03	−3.75
−OH	−6.31	−5.80	−4.35	−4.02
$-OCH_3$	−6.27	−5.90	−4.23	−3.94
$-CH_3$	−6.38	−5.78	−4.28	−3.99
$-CHCH_2$	−6.93	−6.32	−4.67	−4.22
−H	−6.63	−6.05	−4.49	−4.16
$-SCH_3$	−7.10	−6.46	−4.48	−4.20
−F	−7.04	−6.42	−4.88	−4.51
−SH	−7.21	−6.45	−4.94	−4.49
−CCH	−7.36	−6.60	−5.03	−4.56
−Cl	−7.28	−6.48	−5.05	−4.51
−COOH	−7.91	−6.96	−5.40	−4.84
$-COCH_3$	−7.85	−6.92	−5.33	−4.70
$-CF_3$	−7.93	−7.28	−5.58	−5.12
−CN	−8.40	−7.45	−5.93	−5.44
$-NO_2$	−8.89	−7.64	−6.25	−5.36

TABLE 4: Hydrogen Bonding Interaction Energies between the Phenoxyl Radical Cation and Ammonia (kcal/mol)

substituent	$X-C_6H_4-O-H^{\bullet+}\cdots NH_3$		$X-C_6H_4-O^{\bullet}\cdots H-NH_3^+$	
	(U)B3LYP/6-31++g**// (U)B3LYP/6-31++g**	ROMP2/6-311++g**// (U)B3LYP/6-31++g**	(U)B3LYP/6-31++g**// (U)B3LYP/6-31++g**	ROMP2/6-311++g**// (U)B3LYP/6-31++g**
$-N(CH_3)_2$	−17.94	−15.80		
$-NH_2$	−20.29	−18.72		
−OH	−22.78	−21.23	−22.78	−21.34
$-OCH_3$	−22.06	−20.67		
−CH3			−23.78	−23.10
$-CHCH_2$			−24.85	−23.04
−H			−27.73	−27.27
$-SCH_3$	−27.13	−26.94		
−F			−27.93	−27.01
−SH	−29.02	−27.17		
−CCH			−23.33	−22.86
−Cl			−26.10	−25.28
−COOH			−28.87	−28.88
$-COCH_3$			−26.67	−28.08
$-CF_3$			−30.87	−31.21
−CN			−29.91	−30.20
$-NO_2$[a]				

[a] Optimization fails to converge.

in the only minimum on the potential surface. Our own calculation recently at UB3LYP/6-31+g* level also gave the same result.[17] Herein, our calculation at UB3LYP/6-31++g** level again indicated that the proton-transferred $C_6H_5-O^{\bullet}\cdots NH_4^+$ structure is the only minimum for the phenol radical cation−ammonia complex (Table 4).

The binding energy of the transferred $C_6H_5-O^{\bullet}\cdots NH_4^+$ complex is calculated to be 27.73 and 27.27 kcal/mol at UB3LYP/6-31++g** and ROMP2/6-311++g** levels. The same binding energy was estimated before to be 24.3−32.2 kcal/mol using B3LYP and MP2 methods with various basis sets.[9,13] Therefore, we believe that our results are reasonably accurate.

Interestingly, the substitution substantially changes the shape of the potential energy surface of the phenol radical cation−ammonia complex. With para $N(CH_3)_2$, NH_2, OCH_3, SCH_3, and SH substituents, the non-proton-transferred form ($X-C_6H_4-O-H^{\bullet+}\cdots NH_3$) is found to be the only minimum. It should be mentioned that the proton affinities of the corresponding phenoxyl radicals are from 233.7 to 214.4 kcal/mol (ROMP2/6-311++g**).

The only complex having both the $X-C_6H_4-O-H^{\bullet+}\cdots NH_3$ and $X-C_6H_4-O^{\bullet}\cdots NH_4^+$ forms as the minima on the potential energy surface is found to be the para-OH substituted phenol. $HO-C_6H_4-O^{\bullet}$ has a proton affinity of 211.7 kcal/mol (ROMP2).

TABLE 5: Hydrogen Bonding Interaction Energies between the Phenoxyl Radical Cation and Water (kcal/mol)

substituent	$X-C_6H_4-O-H^{\bullet+}\cdots OH_2$	
	(U)B3LYP/6-31++g**// (U)B3LYP/6-31++g**	ROMP2/6-311++g**// (U)B3LYP/6-31++g**
$-N(CH_3)_2$	−13.22	−11.82
$-NH_2$	−14.75	−13.59
−OH	−16.07	−15.09
$-OCH_3$	−15.73	−14.83
$-CH_3$	−17.07	−16.25
$-CHCH_2$	−15.57	−14.63
−H	−18.49	−17.62
$-SCH_3$	−14.57	−13.09
−F	−18.64	−17.56
−SH	−15.66	−14.44
−CCH	−16.47	−15.91
−Cl	−17.77	−17.48
−COOH	−18.80	(−11.07)[a]
$-COCH_3$	−17.32	−17.85
$-CF_3$	−19.65	−18.93
−CN	−19.17	−18.45
$-NO_2$	−19.83	−19.36

[a] This value is obviously peculiar compared to its neighbors, although it is reproducible. It is not used in regression analysis.

All the remaining phenol radical cation−ammonia complexes have the proton-transferred form as the minimum. The proton affinities of the corresponding phenoxyl radicals are from 210.2 to 191.9 kcal/mol (ROMP2).

TABLE 6: Gas-Phase Adiabatic Ionization Potentials (eV) of the Hydrogen-Bonded Phenol−Water Complexes and Phenol−Ammonia Complexes

	ammonia		water	
substituent	(U)B3LYP/6-31++g**//(U)B3LYP/6-31++g**	ROMP2/6-311++g**//(U)B3LYP/6-31++g**	(U)B3LYP/6-31++g**//(U)B3LYP/6-31++g**	ROMP2/6-311++g**//(U)B3LYP/6-31++g**
$-N(CH_3)_2$	6.10	6.20	6.22	6.30
$-NH_2$	6.39	6.56	6.54	6.69
−OH	6.91	7.00	7.13	7.24
$-OCH_3$	6.75	6.88	6.94	7.06
$-CH_3$	6.78	6.89	7.34	7.50
$-CHCH_2$	6.81	6.97	7.13	7.30
−H	7.34	7.40	7.65	7.79
$-SCH_3$	6.74	6.89	6.84	6.94
−F	7.36	7.38	7.68	7.76
−SH	6.66	6.79	7.15	7.26
−CCH	7.19	7.33	7.40	7.59
−Cl	7.36	7.39	7.64	7.72
−COOH	7.65	7.64	7.99	(10.36)
$-COCH_3$	7.57	7.60	7.88	7.99
$-CF_3$	7.77	7.79	8.16	8.27
−CN	7.79	7.81	8.15	8.27
$-NO_2$			8.45	8.38

Therefore, depending on the proton affinity (PA) of the phenoxyl radical, either the non-proton-transferred form is the only minimum (when PA > 214.4 kcal/mol), or the proton-transferred form is the only minimum (when PA < 210.2 kcal/mol), or both the non-proton-transferred and proton-transferred forms are minima. This observation can be rationalized if one notices that the proton affinity of ammonia is 203.9 kcal/mol. Thus, a subtle change of the proton affinity associated with the proton donor may completely change the shape of potential energy surface when the proton affinities of the donor and acceptor are close to each other. It should be mentioned that the change of the proton affinity of the proton acceptor can also completely change the shape of the potential energy surface, which was shown in our recent study on the complexes between phenol radical cation and various amines.[17] It was found there that when the amine has a proton affinity larger than 204 kcal/mol, the complex between unsubstituted phenol radical cation and amine has the proton-transferred form as the only minimum. When the proton affinity of the amine is in the range of 190−197 kcal/mol, both the proton-transferred and non-proton-transferred structures are minima. When the proton affinity of the amine is smaller than 189 kcal/mol, no proton transfer can take place.

Despite the fact that the shape of the potential surfaces changes, the binding energies between the substituted radical cation and ammonia follow the Hammett relationship:

$$D_{\text{phenol radical cation}-\text{ammonia}}(\text{UB3LYP}) = -25.4 - 7.6\sigma_p (r = 0.88) \quad (14)$$

$$D_{\text{phenol radical cation}-\text{ammonia}}(\text{ROMP2}) = -24.6 - 9.3\sigma_p (r = 0.92) \quad (15)$$

Clearly, the slope here is much larger than that for the complexes between phenols and ammonia.

The proton affinity of water is 164.5 kcal/mol (ROMP2), which is much smaller than those for all the phenoxyl radicals. Therefore, it is understandable that all the phenol radical cation−water complexes have only one minimum corresponding to the non-proton-transferred form. This result agrees with the previous findings.[9,13] The binding energy between phenol radical cation and water is calculated to be 18.49 or 17.62 kcal/mol at UB3LYP/6-31++g** or ROMP2/6-311++g** level. These values are in agreement with the experimental binding energy, 18.54 kcal/mol.[8] In addition, the Hammett analyses on the phenol radical cation−water complexes give the following equations:

$$D_{\text{phenol radical cation}-\text{water}}(\text{UB3LYP}) = -16.7 - 3.6\sigma_p (r = 0.88) \quad (16)$$

$$D_{\text{phenol radical cation}-\text{water}}(\text{ROMP2}) = -15.8 - 4.1\sigma_p (r = 0.92) \quad (17)$$

Putting all the slopes together, we find that they decrease in the order phenol−water complex < phenol−ammonia complex < phenol radical cation−water complex < phenol radical cation−ammonia complex. Clearly, this order is the same as that for the binding energies.

3.4. Effects of Hydrogen Bonding on the Oxidation of Phenols. The hydrogen bonding to water or ammonia decreases the adiabatic oxidation potential of phenols (Table 6). For example, when hydrogen bonded to ammonia, the oxidation potential of phenol is calculated to be 7.34 or 7.40 eV at UB3LYP/6-31++g** or ROMP2/6-311++g** level. The same potential was also estimated before at B3LYP/D95++** level to be 7.33 eV.[13] Therefore, ammonia causes a decrease of 0.93 or 1.01 eV for the oxidation potential of phenol (Table 7). Water is less effective than ammonia for lowering the oxidation potential. At UB3LYP/6-31++g** or ROMP2/6-311++g** level, the oxidation potential for phenol−water complex is calculated to be 7.65 or 7.79 eV. The same potential was also estimated to be 7.65 eV before at B3LYP/D95++** level.[13] Therefore, water causes a decrease of 0.62 eV for the oxidation potential of phenol. For all the other substituted phenols, it is found that the adiabatic oxidation potentials follow the Hammett relationship as shown in the following equations:

$$\text{IP}_{\text{phenol}-\text{ammonia}}(\text{UB3LYP}) = 7.0 + 1.1\sigma_p (r = 0.90) \quad (18)$$

$$\text{IP}_{\text{phenol}-\text{ammonia}}(\text{ROMP2}) = 7.1 + 1.0\sigma_p (r = 0.91) \quad (19)$$

$$\text{IP}_{\text{phenol}-\text{water}}(\text{UB3LYP}) = 7.3 + 1.3\sigma_p (r = 0.93) \quad (20)$$

$$\text{IP}_{\text{phenol}-\text{water}}(\text{ROMP2}) = 7.4 + 1.2\sigma_p (r = 0.92) \quad (21)$$

TABLE 7: Changes of the Gas-Phase Adiabatic Ionization Potentials (eV) upon Hydrogen Bonding to Water or Ammonia for Substituted Phenols[a]

	ammonia		water	
substituent	(U)B3LYP/6-31++g**// (U)B3LYP/6-31++g**	ROMP2/6-311++g**// (U)B3LYP/6-31++g**	(U)B3LYP/6-31++g**// (U)B3LYP/6-31++g**	ROMP2/6-311++g**// (U)B3LYP/6-31++g**
$-N(CH_3)_2$	0.53	0.47	0.41	0.37
$-NH_2$	0.63	0.60	0.48	0.47
$-OH$	0.73	0.76	0.52	0.51
$-OCH_3$	0.70	0.68	0.51	0.50
$-CH3$	1.12	1.18	0.57	0.57
$-CHCH_2$	0.79	0.81	0.48	0.48
$-H$	0.93	1.01	0.62	0.62
$-SCH_3$	0.57	0.53	0.47	0.47
$-F$	0.92	0.98	0.61	0.60
$-SH$	0.96	0.93	0.47	0.46
$-CCH$	0.71	0.79	0.51	0.52
$-Cl$	0.83	0.90	0.56	0.57
$-COOH$	0.93	1.04	0.59	(−1.68)
$-COCH_3$	0.83	1.00	0.53	0.60
$-CF_3$	1.01	1.12	0.62	0.64
$-CN$	0.95	1.07	0.59	0.60
$-NO_2$			0.60	0.64

[a] Calculated as $\Delta I = I_{\text{phenol complex}} - I_{\text{free phenol}}$.

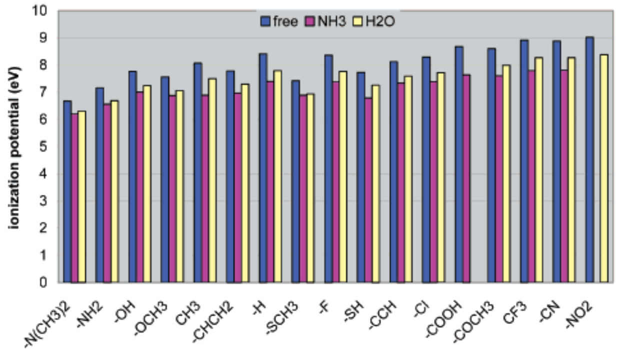

Figure 3. Ionization potentials of the free phenols and phenol complexes of ammonia or water.

As the slopes of the above equations are smaller than that (1.4 eV) for the adiabatic oxidation potentials of uncomplexed substituted phenols, we expect that the ammonia or water hydrogen bonding effect on the oxidation potential is different for different substituents. Indeed, as shown in Table 7 a phenol substituted with a more electron-withdrawing group generally shows larger reduction in the adiabatic oxidation potential when hydrogen bonded to water or ammonia. The slopes for the reduction are calculated to be 0.2 eV for ammonia complexes and 0.1 eV for water complexes.

4. Conclusion

We have done a fairly large amount of calculations using reliable levels of methods on the hydrogen bonding of a number of substituted phenols or their radical cations with water or ammonia. The results should be highly valuable for the experimentalists caring about the events taking place in the gas phase. The results should also be fairly helpful for the chemists considering how to tune the redox in solution. Although no unexpected behavior has been identified, we have collected useful quantitative results including the following:

1. The magnitudes of the proton affinities increase in the order water (165 kcal/mol) < ammonia (204 kcal/mol) ≈ phenoxyl radicals (193−235 kcal/mol) < phenolate anions (321−352 kcal/mol). The slopes of the proton affinities against the substituent σ_p constants are about 22 and 15 kcal/mol for phenoxyl radicals and phenolate anions.

2. The slopes of the binding energies against the substituent σ_p constants decrease in the order phenol−water complex (1.1 kcal/mol) < phenol−ammonia complex (1.4 kcal/mol) < phenol radical cation−water complex (4.1 kcal/mol) < phenol radical cation−ammonia complex (9.3 kcal/mol). The stronger the hydrogen bonding, the larger the substituent effects.

3. The structure of the phenol radical cation−ammonia complex relies on the proton affinity of the phenoxyl radical. When the proton affinity is larger than 214 kcal/mol, the non-proton-transferred form is the only minimum on the potential energy surface. When the proton affinity is smaller than 210 kcal/mol, the proton-transferred form is the only minimum. The only complex for which both the proton-transferred and non-proton-transferred forms are minima is that of *p*-hydroxyphenol radical cation.

4. All the phenol radical cation complexes with water have the non-proton-transferred form as the only minimum on the potential surface.

5. Hydrogen bonding to ammonia lowers the adiabatic oxidation potentials of phenols by 0.5−1.2 eV. Hydrogen bonding to water lowers the adiabatic oxidation potentials of phenols by 0.4−0.6 eV. In general, a phenol substituted with a more electron-withdrawing group shows larger reduction in the adiabatic oxidation potential when complexed to water or ammonia.

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