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Proton Affinities of Free Radicals Measured by the Kinetic Method

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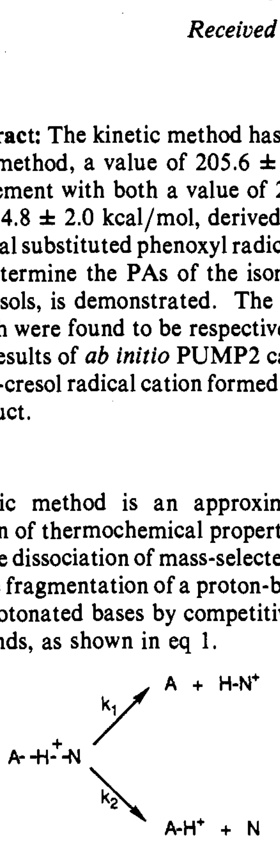
Abstract: The kinetic method has been applied to the determination of proton affinities (PAs) of free radicals. Using this method, a value of 205.6 ± 0.3 kcal/mol for the PA of the phenoxyl radical is obtained. This PA is in good agreement with both a value of 204.4 ± 2.0 kcal/mol, determined by FT-ICR bracketing experiments, and a value of 204.8 ± 2.0 kcal/mol, derived from published experimental data, by use of a thermochemical cycle. The PAs of several substituted phenoxyl radicals were also determined by the kinetic method. In addition, the ability of the method to determine the PAs of the isomeric radicals, methylphenoxyl and hydroxybenzyl, each derived from *o*-, *m*-, and *p*-cresols, is demonstrated. The PAs determined for the isomeric *p*-methylphenoxyl and *p*-hydroxybenzyl radicals, which were found to be respectively 5.1 and 9.0 kcal/mol higher than the PA of phenoxyl radical, were supported by the results of *ab initio* PUMP2 calculations, performed with the 6-31G** basis set. The calculations also found that the *p*-cresol radical cation formed by protonation of either of these isomeric radicals is the thermodynamically preferred product.

The kinetic method is an approximate method for the determination of thermochemical properties, based on the rates of competitive dissociation of mass-selected cluster ions.[1] A case in point is the fragmentation of a proton-bound dimer to give the individual protonated bases by competitive cleavage of the two hydrogen bonds, as shown in eq 1.



(1)

The method is limited to systems where the rates of fragmentation of weakly bound cluster ions, which can be the result of metastable or collision-induced dissociation, depend only on the critical energies of the two competitive processes because entropic effects are either negligible or they cancel. The method also requires that secondary dissociations do not occur to a significant extent so that the abundances of NH^+ and AH^+ will indicate the relative proton affinities of the respective bases.[1] When these considerations apply, the kinetic method gives results which agree well with other methods for determining the proton affinities of simple carboxylic acids, amines, alcohols, amino acids, and pyridines.[1–6] The method has also been applied to estimate ammonium ion,[7] metal ion,[8–10] electron,[11] and chlorine cation affinities.[12] It is very sensitive to small thermochemical differences, and the kinetic method finds application in circumstances where conventional techniques are inapplicable. For example, it can be used with impure or non-volatile samples.

In this paper, we extend the kinetic method to the measurement of the thermochemical properties of free radicals. Provided a weakly bound cluster ion of the type A- -H⁺- -N can be formed, where A is a free radical and N is a reference compound of known proton affinity (PA), it should be possible to measure the PA of A by the same method used to measure the PAs of closed-shell neutral molecules. Weakly bound cluster ions of this type have recently been proposed to form under chemical ionization conditions with appropriate systems. Vairamani *et al.*[13] suggest the formation of a proton-bound dimer of phenoxyl radical and acetone, when acetone is used as a reagent gas for chemical ionization. Evidence for this type of structure is obtained through collision-induced dissociation, both in the radical case[13] and in closed-shell systems. These cluster ions fragment very efficiently at low collision energies and pressures to give two product ions, which arise from a competition between the two possible modes of hydrogen bond cleavage.

In this study, the applicability of the kinetic method to radical PA measurements was examined, using the phenoxyl radical as a test case. Chemical ionization of phenol, using a reagent gas which has a PA similar to that of phenoxyl radical, results in the formation of a proton-bound dimer between phenoxyl radical and the reagent gas. A variety of reagent gases, N, each of known PA, were used to establish a correlation line based on the relationship defined in eq 2.

$$\ln(NH^+/AH^+) \approx \Delta PA/RT \qquad (2)$$

This relationship has been derived elsewhere.[1,3]

In eq 2, NH^+/AH^+ is the ratio of the peak intensities of the protonated reagent gas to the protonated phenoxyl radical, R is the gas constant, and T is the effective temperature of the proton-

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bound dimers. This temperature is not an external temperature, since the dissociating proton-bound dimer ions have non-Boltzmann distributions of internal energies.[1] A plot of ln(NH^+/AH^+) vs the PAs of the reagent gases, N, should result in a straight line with a slope of $1/RT$ and an x intercept that corresponds to the PA of phenoxyl radical.

The method was also used to measure the PAs of substituted phenoxyl radicals, for which experimental values were previously unavailable. The experimentally determined PAs were compared with those derived from *ab initio* UHF and PUMP2 calculations, using the 6-31G** basis set.[14]

In addition to illustrating the applicability of the kinetic method to the determination of the PAs of free radicals, the experimental results demonstrate that the application of this method allows one to measure the thermochemical properties of *local sites* in molecules. The PAs of the *o*-, *m*-, and *p*-methylphenoxyl radicals and their isomers, the *o*-, *m*-, and *p*-hydroxybenzyl radicals, have been measured. Proton-bound dimers consisting of each of these radical isomers and various reagent gases were generated by chemical ionization of *o*-, *m*-, and *p*-cresol (methylphenol). *Ab initio* calculations were used to show that the two different PAs measured in the experiments with *p*-cresol correspond to those expected for *p*-methylphenoxyl and *p*-hydroxybenzyl radicals and to establish which radical is associated with each PA.

Experimental Section

Experiments were performed using a Finnigan Triple Stage Quadrupole (TSQ) 700 mass spectrometer (Finnigan MAT, San Jose, CA). Reagent gases of known PA were introduced into the source through the GC inlet with a Granville Phillips (Granville Phillips Co., Boulder, CO) variable leak valve at sufficient pressure to create chemical ionization conditions in the source. Reagent gases with high boiling points were heated to provide appropriate source pressures. The source temperature was maintained at 100 °C and the manifold at 70 °C throughout the experiments. Aliquots (1 μL) of phenol, *p*-fluorophenol, and *o*-, *m*-, and *p*-cresol were deposited from a methanol solution (1 M) onto the filament of a direct evaporation probe. The direct evaporation probe was not heated; the sample was allowed to evaporate in the source during the experiment. This procedure provided adequate signal for the proton-bound, radical dimers for 10–30 s.

Ions corresponding to the mass-to-charge ratio of the proton-bound, radical dimers were mass selected using quadrupole 1. Collisional activation in quadrupole 2 employed very mild conditions, viz. 4 eV collision energy and an argon target at a nominal pressure of 0.4 mTorr. The ratios of the product ions were then obtained from the spectra generated by scanning quadrupole 3.

The partial pressure of each gas is critical for the production of a proton-bound dimer which dissociates efficiently with little secondary fragmentation. The source conditions were optimized to give the maximum signal intensity of product ions arising from the proton-bound dimer before peak ratios were measured. Each set of peak ratios was measured from an average of 15 or more scans. Peak ratio measurements were taken in triplicate for the phenoxyl and *p*-fluorophenoxyl radicals and displayed relative standard deviations of less than 5%. Peak ratios for the measurement of the PAs of the *o*-, *m*-, and *p*-cresol radicals were recorded in duplicate, again with relative standard deviations of less than 5%. The natural logarithm of the peak ratios was plotted versus the PAs of the reagent gases, and the best straight line was determined by a least-squares regression analysis. The PA of each radical was taken as the x intercept and the effective temperature of the proton-bound dimer, from which it was formed, was obtained from the slope. Errors for the proton affinities determined in this study are estimated values.[15]

Computational Methodology

Ab initio calculations were performed with Gaussian 92.[16] Geometries were optimized with UHF/6-31G** calculations and are available as supplementary material.[17] Energies at these geometries were recalculated at the MP2/6-31G** level.

For UHF wave functions, like those in this study, that have large amounts of spin contamination (e.g. S^2 = 1.37–1.39 for the phenoxyl and benzyl radicals and S^2 = 0.95–1.02 for phenol radical cations, versus 0.75 for pure doublets), unrestricted (U)MP2 energies are much less reliable than those obtained after projection of the lowest spin contaminant (PUMP2).[18] However, even after projection of the quartet contaminants from the UHF wave functions, S^2 = 1.10–1.12 for the radicals, whereas S^2 = 0.75–0.80 for the radical cations. Differences between the values of S^2 for the wave functions for the radicals and radical cations should, of course, have a much smaller effect on the calculations of the relative PAs than on the absolute PAs computed.

Results

The PA of phenoxyl radical is known with considerable certainty. It has been measured experimentally by DeFrees *et al.* in Fourier-transform ion cyclotron resonance (FT-ICR) bracketing experiments.[19] In addition, the data necessary to calculate the PA of phenoxyl radical, using a thermochemical cycle, are available.[20,21] The reagent gases needed for measurement of its PA by the kinetic method were chosen to have PAs similar to that expected for phenoxyl radical, so that competitive fragmentation would allow eq 2 to be used with the greatest possible accuracy. To minimize differences in entropic effects on reaction rates, it is desirable that the proton binding sites in the reagent gases be chemically similar to that in phenoxyl radical. For this reason, ethers and ketones with PAs ranging from 202.3 to 208.7 kcal/mol were chosen. Values for the PAs of the reagent gases were taken from ref 22.

Collision-induced dissociation of the mass-selected dimers under mild activation conditions generated two fragment ions, due to the competitive dissociations with rate constants k_1 (the rate at which the reagent gas takes the proton) and k_2 (the rate at which phenoxyl radical takes the proton). An example of the type of product ion spectrum recorded is shown in Figure 1, where the reagent gas is acetophenone.

Table 1 lists the PAs of the reagent gases and the natural logarithm of the measured ion abundance ratios. A plot of the natural logarithm of the ion abundance ratios versus the PAs of the known compounds is shown in Figure 2. From these data, the PA of phenoxyl radical is estimated to be 205.6 ± 0.3 kcal/mol and the effective temperature of the dimer is 423 K, r = 0.995 (Table 3).

In further experiments, the PA of the *p*-fluorophenoxyl radical was estimated in the same way as the PA of the phenoxyl radical. Table 1 summarizes the natural logarithm of peak ratios determined in these experiments. As shown in Table 3, the PA of *p*-fluorophenoxyl radical is estimated to be 204.5 ± 0.3 kcal/mol and the effective temperature of the dimer is 399 K, r = 0.980.

To check the reasonableness of this experimental result, *ab initio* calculations of the PAs of the phenoxyl and *p*-fluorophenoxyl

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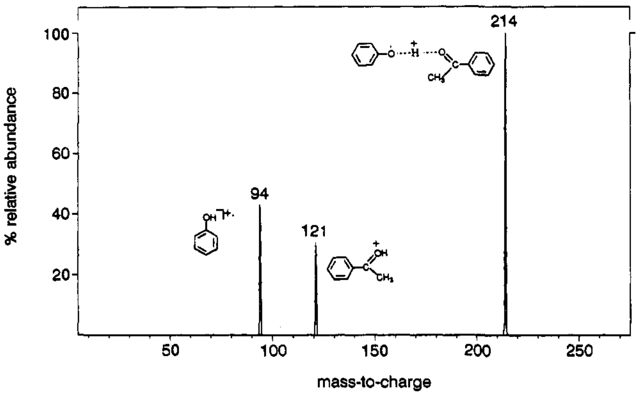


Figure 1. MS/MS product ion spectrum of the mass-selected proton-bound dimer composed of phenoxyl radical and acetophenone. Activation was achieved with 4-eV collisions on an argon target at a pressure of 0.4 mTorr.

Table 1. Natural Logarithm of the Ion Abundance Ratios of the Product Ions Generated from the Phenoxyl and *p*-Fluorophenoxyl Radical Proton-Bound Dimers with Various Reference Compounds

ref compd	PA (kcal/mol)	ln ratio	
		phenol	*p*-fluorophenol
n-propyl ether	202.3	−3.86	−2.76
n-butyl ether	203.7	−2.16	−1.00
n-pentyl ether[a]	205.2	−1.08	0.17
acetophenone	205.4	−0.37	1.24
isopropyl ether	206.0	0.61	2.18
ethyl vinyl ether	208.2	3.21	
p-methylacetophenone	208.7	3.62	

[a] Data reported in ref 22 for this compound are those given by the original author and are not necessarily internally consistent.

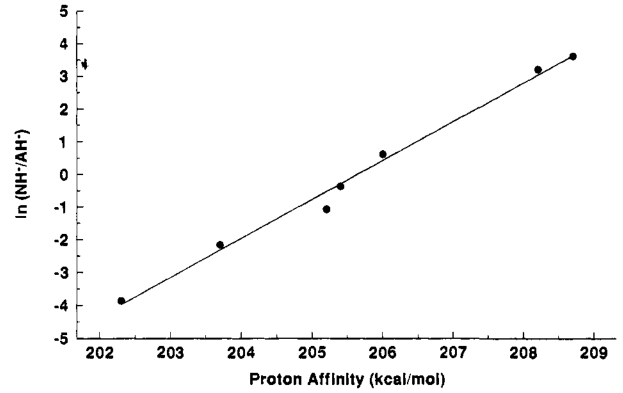


Figure 2. Natural logarithm of the ion abundance ratios versus the PAs of the reagent gases used in the determination of the PA of phenoxyl radical. The peak ratios were determined in triplicate with relative standard deviations of less than 5%.

Table 2. Natural Logarithm of the Ion Abundance Ratios of the Product Ions Generated from the *o*-, *m*-, and *p*-Cresol Radical Proton-Bound Dimers with Various Reference Compounds

ref compd	PA (kcal/mol)	ln ratio		
		o-cresol	*m*-cresol	*p*-cresol
acetophenone	205.4	−4.85		
isopropyl ether	206.0	−3.40	−3.87	
2,4-pentanedione	207.8	−2.39	−3.16	−4.89
ethyl vinyl ether	208.2	0.78	−0.28	−1.68
p-methylacetophenone	208.7	−0.33	−1.10	−3.18
pyrazine	209.0	2.06	1.09	−0.34
2-fluoropyridine	210.6	3.21	1.71	−0.04
dimethyl sulfoxide	211.3	2.53	1.72	0.14
1,4-butanediol[a]	212.0	−0.27	−1.05	−2.73
2,5-hexanedione	213.2	1.40	0.92	−0.69
4-methoxybenzaldehyde	213.5	0.72	−0.41	−2.56
3-fluoropyridine	214.3	2.91	1.72	0.05
ethyl amine	217.0			2.88
n-propyl amine	217.9			3.66

[a] Data reported in ref 22 for this compound are those given by the original author and are not necessarily internally consistent.

Table 3. Experimental Proton Affinities and Effective Temperatures Determined by the Kinetic Method

radical	PA (kcal/mol)	T_{eff} (K)
phenoxyl	205.6 ± 0.3	423
p-fluorophenoxyl	204.5 ± 0.3	399
o-methylphenoxyl	208.6 ± 1.0	368
o-hydroxybenzyl	212.3 ± 1.0	392
m-methylphenoxyl	209.3 ± 1.0	431
m-hydroxybenzyl	213.0 ± 1.0	463
p-methylphenoxyl	210.7 ± 1.0	435
p-hydroxybenzyl	214.6 ± 1.0	450

Table 4. UHF and PUMP2 Energies (hartrees), Calculated with the 6-31G** Basis Set at UHF/6-31G** Optimized Geometries, and Zero-Point Energies (kcal/mol), Obtained from UHF/6-31G** Vibrational Analyses

species	*E*		
	UHF	PUMP2	zero-point
phenoxyl	−304.9839	−305.9028	60.0
phenol$^{\bullet+}$	−305.3206	−306.2412	69.7
C_4-protonated phenoxyl	−305.2774	−306.1806	69.0
p-fluorophenoxyl	−403.8319	−404.9121	54.8
p-fluorophenol$^{\bullet+}$	−404.1622	−405.2499	64.7
p-methylphenoxyl	−344.0247	−345.0903	78.4
p-hydroxybenzyl	−344.0109	−345.0812	78.2
p-cresol$^{\bullet+}$	−344.3683	−345.4382	88.2
O-protonated *p*-hydroxybenzyl	−344.3180	−345.3919	86.2

Table 5. Comparison of Measured and Calculated[a] PAs (kcal/mol), Relative to That of Phenoxyl

radical	PA	
	measured	calculated
phenoxyl	0[b]	0[c]
p-fluorophenoxyl	−1.1	−0.6
p-methylphenoxyl	5.1	5.9
p-hydroxybenzyl	9.0	11.4

[a] PUMP2/6-31G**//UHF/6-31G**, after correction for zero-point energy differences. [b] Relative to 205.6 ± 0.3 kcal/mol, measured for phenoxyl. [c] Relative to 202.6 kcal/mol, calculated for phenoxyl.

radicals were performed. The UHF, PUMP2, and zero-point energies are given in Table 4. After correction for the large zero-point energy difference between phenoxyl radical and phenol radical cation, the PAs computed at the UHF and PUMP2 levels are respectively 201.6 and 202.7 kcal/mol. Both computational methods give a PA for phenoxyl radical that is only slightly smaller than the experimental value of 205.6 ± 0.3 kcal/mol, although differences and not absolute values can be expected to be given accurately by the computations.

The value computed for the PA of *p*-fluorophenoxyl, relative to that of phenoxyl, requires a correction of only 0.2 kcal/mol for zero-point energy differences. After this very small correction, the PA of *p*-fluorophenoxyl was computed to be less than that of phenoxyl by 4.2 kcal/mol at the UHF level, but by only 0.6 kcal/mol at the higher, PUMP2 level of theory. Thus, as shown in Table 5, the PUMP2 results confirm the very small decrease in PA, found experimentally, upon addition of a *p*-fluoro substituent to phenoxyl radical.

The ability of the kinetic method to yield PAs of isomeric radicals, formed from a common neutral species, is demonstrated by the measurements of the PAs of the methylphenoxyl and hydroxybenzyl radicals, each generated from *o*-, *m*-, and *p*-cresol. Because the PAs of these free radicals are several kilocalories per mole higher than the PA of phenoxyl radical, there is not a

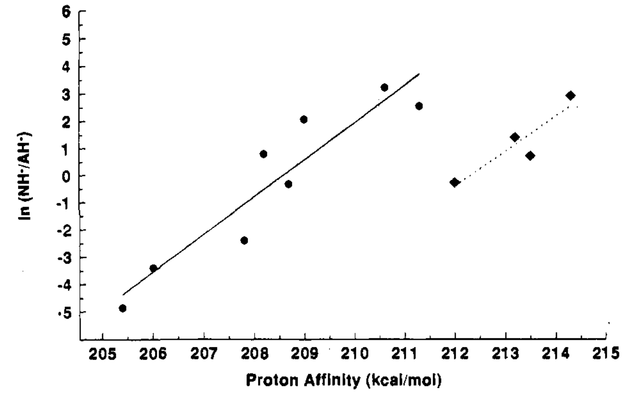


Figure 3. Natural logarithm of the ion abundance ratios versus the PAs of the reagent gases used in the determination of the PAs of *o*-methylphenoxyl and *o*-hydroxybenzyl radicals, both generated from *o*-cresol. The solid line is assigned to the *o*-methylphenoxyl radical, and the dashed line is assigned to its *o*-hydroxybenzyl isomer.

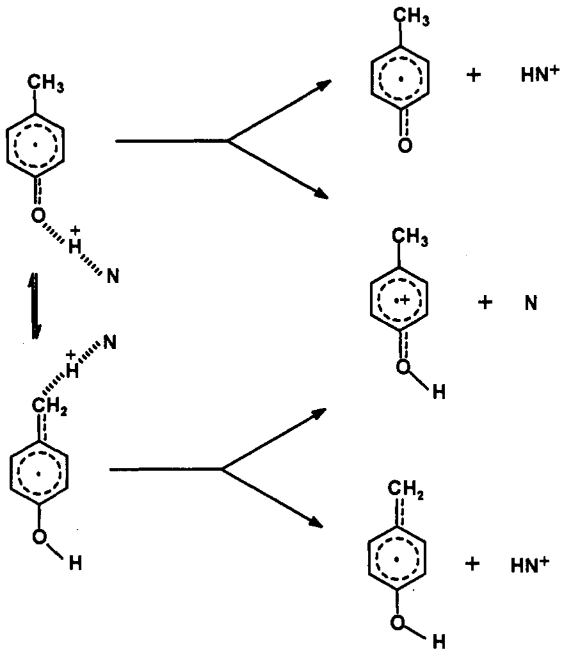
sufficient number of simple ethers and ketones with PAs in this higher range. Therefore, compounds with different types of basic sites, as well as polyfunctional compounds, had to be used as references. The use of reagent gases with a variety of functional groups should still provide an accurate measure of PAs, but this is expected to add some scatter to the plot of the natural log of the ion-abundance ratios versus the PAs of the reagent gases. The raw data for the determination of the PAs of the radicals formed from *o*-, *m*-, and *p*-cresol are summarized in Table 2; and the PAs for the radicals, along with the effective temperatures of the dimers from which they are formed, are displayed in Table 3.

The plot for the determination of the PA of the radical(s) formed by H• loss from *o*-cresol is shown in Figure 3. This plot reveals the presence of two lines. On the basis of the computational results described below, the solid line is assigned to the *o*-methylphenoxyl radical. As summarized in Table 3, the experimental data show that this species has a PA of 208.6 ± 1.0 kcal/mol and that the activated dimer has an effective temperature of 368 K, $r = 0.935$. The dashed line in Figure 3 is assigned to the *o*-hydroxybenzyl radical. The PA of this compound is determined to be 212.3 ± 1.0 kcal/mol, and the dimer that gives rise to this radical has an effective temperature of 392 K, $r = 0.916$.

Two separate lines were also observed in the plots used to determine the PAs of the radicals formed from *m*- and *p*-cresol; the lines were again attributed to the formation of two isomeric free radicals. In the experiments with both *m*- and *p*-cresol, as in those with *o*-cresol, the lower PA was assigned to the methylphenoxyl radical and the higher to its hydroxybenzyl isomer. The PA was determined to be 209.3 ± 1.0 kcal/mol for the *m*-methylphenoxyl radical and 213.0 ± 1.0 kcal/mol for the *m*-hydroxybenzyl radical. The corresponding PAs of the radicals derived from *p*-cresol are both slightly higher, 210.7 ± 1.0 kcal/mol for *p*-methylphenoxyl and 214.6 ± 1.0 kcal/mol for *p*-hydroxybenzyl.

Ab initio calculations of the PAs of the isomeric *p*-methylphenoxyl and *p*-hydroxybenzyl radicals were performed. The calculated PAs are compared in Table 5 to those measured by the kinetic method. The PA of *p*-methylphenoxyl is calculated to be 5.9 kcal/mol greater than that of phenoxyl, whereas the experimental measurement shows a 5.1 kcal/mol increase. The calculations predict the PA of *p*-hydroxybenzyl radical to be 5.5 kcal/mol greater than that of its *p*-methylphenoxyl isomer, compared to the experimental difference of 3.9 kcal/mol. The agreement between the calculated differences in PAs and those measured by the kinetic method provides strong support for the interpretation of the experimental results in terms of the formation of two isomeric radicals.

Scheme 1. Formation of Isomeric *p*-Methylphenoxyl and *p*-Hydroxybenzyl Radicals by Fragmentation of the Proton-Bound Dimers of *p*-Cresol Radicals and Reagent Gas, N



The calculations also indicate that the *p*-methylphenoxyl radical has a lower PA than its *p*-hydroxybenzyl isomer. This provides the basis for assigning the methylphenoxyl structure to the radical of lower PA in the experiments with each of the cresols. Since, as shown in Scheme 1 for *p*-methylphenoxyl and *p*-hydroxybenzyl, both isomeric radicals are expected to give the same cresol radical cation upon protonation, the difference between the PAs of each pair of isomeric radicals is equal to the difference between the enthalpies of the two radicals.

Calculations were performed in order to verify that formation of *p*-cresol radical cation would be thermodynamically favored upon protonation of both *p*-methylphenoxyl and *p*-hydroxybenzyl radicals. This was, in fact, confirmed to be the case. For example, after correction for zero-point energy differences, the PUMP2/6-31G** calculations found protonation of phenoxyl at C_4 to form the radical cation of 2,5-cyclohexadien-1-one[23] to be 37.3 kcal/mol less favorable than protonation at oxygen to form the radical cation of phenol. Similarly, protonation of *p*-hydroxybenzyl radical on oxygen to form a distonic radical cation was computed to be 27.5 kcal/mol less favorable than protonation on carbon to form *p*-cresol radical cation.

Discussion

The value of 205.6 ± 0.3 kcal/mol, obtained by the kinetic method, for the PA of phenoxyl radical is in good agreement with the value of 204.4 ± 2.0 kcal/mol, obtained by the FT-ICR bracketing experiments of Defrees *et al.*[19] As an independent check on both experiments, the PA of phenoxyl radical was calculated via a thermochemical cycle from the ionization energy of phenol (8.47 eV[20]), the bond dissociation energy (BDE) of the C_6H_5O–H bond (86.5 kcal/mol[21]), and the ionization energy of the hydrogen atom (13.598 eV[20]). A value of 204.8 kcal/mol is thus obtained, with an estimated uncertainty of ±2.0 kcal/mol. Clearly, the kinetic method provides an accurate value for the PA of phenoxyl radical.

The addition of a fluoro substituent at the *para* position of phenoxyl radical has a very small effect on the PA. As shown

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(23) C_4-protonated phenoxyl was the only species, on which calculations were performed in this study, that was found to have the unpaired electron in a σ, rather than in a π, orbital.

in Table 5, both the kinetic experiments and the PUMP2 calculations find a decrease on the order of about 1 kcal/mol in the PA of the *p*-fluorophenoxyl radical, relative to the PA of the phenoxyl radical. This is slightly less than half of the effect that a *p*-fluoro substituent has on reducing the PA of the phenolate anion.[24]

The reproducibility of the spectra, especially those used to obtain the PA of phenoxyl and of *p*-fluorophenoxyl, was very good. As noted in the Experimental Section, the peak ratios were measured multiple times and found to have relative standard deviations of less than 5%. Peaks, other than those corresponding to the parent ion and the two product ions, were less than 5% of the base peak in all product ion spectra.

Probably the most interesting result of this study is the finding that the kinetic method can be used to obtain the PAs of two isomeric radicals, formed from the same precursor. Formation of two isomeric radicals by proton loss at two different sites (as illustrated in Scheme 1) is indicated by the observation of two different lines in the plots for the determinations of the PAs of the radicals that are generated from *o*-, *m*-, and *p*-cresol. These two lines are assigned to two isomeric radicals with different PAs.

This interpretation is consistent with thermochemical data which are used to calculate the PAs of the isomeric *p*-methylphenoxyl and *p*-hydroxybenzyl radical isomers via a thermochemical cycle. Because the ionization energies of *p*-cresol (8.13 eV[20]) and atomic hydrogen (13.598 eV[20]) are common to the proton affinity thermochemical cycles of these two isomers, the difference in their proton affinities is equal to the difference in the O–H and C–H bond dissociation energies. These bond dissociation energies are unknown but are expected to be close to those in phenol and toluene, respectively. The O–H bond dissociation energy of phenol is taken from ref 21 to be 86.5 ± 2.0 kcal/mol. A value of 90.4 kcal/mol for the C–H bond dissociation energy of toluene to form benzyl radical has also been reported.[25] This value is slightly larger than that of 87.9 ± 1.5 kcal/mol given in ref 21, but the higher value is supported by the results of *ab initio* calculations.[26] The above data lead to a calculated PA of 212.6 kcal/mol for the *p*-methylphenoxyl radical and a PA of 216.5 kcal/mol for the proton affinity of the *p*-hydroxybenzyl radical. Considering the uncertainties in the thermodynamic data used in the thermochemical cycles, the agreement between the calculated values and the experimental PAs given in Table 3 (210.7 kcal/mol for the *p*-methylphenoxyl radical and 214.6 kcal/mol for the *p*-hydroxybenzyl radical) is excellent. In addition, the calculated difference in isomeric PAs of 3.9 kcal/mol is in exact agreement with the measured difference.

The slopes of the lines in Figure 3 and, hence, the effective temperatures of the dimers from which the isomeric radicals are formed are similar to those in the simpler phenoxyl and *p*-fluorophenoxyl radical cases. Table 3 shows that the effective temperatures for all of the radical species studied range from 368 to 463 K. If one line was drawn through all of the points used for the determinations of the PAs of the radicals formed from each of the cresols, the slopes would indicate internal temperatures for the proton-bound dimers in excess of 750 K. Such a result would not be consistent with the internal temperatures obtained for the proton-bound dimers from which phenoxyl and *p*-fluorophenoxyl radical are formed.

Further evidence for the formation of two isomeric radicals from *p*-cresol comes from the results of the *ab initio* calculations. As noted above, the PUMP2/6-31G**//UHF/6-31G** calculations give relative PAs for phenoxyl, *p*-methylphenoxyl, and *p*-hydroxybenzyl that correspond satisfactorily to those obtained from the experimental data. The computational results also allow the assignment of the lower PA and, hence, the lower energy to *p*-methylphenoxyl, which is computed to be more stable than the isomeric *p*-hydroxybenzyl radical by 5.5 kcal/mol.[27] Finally, the calculations show that *p*-cresol radical cation is considerably lower in energy than other radical cations that might be formed by alternate sites of protonation in these two isomeric radicals.

The existence of two isomeric forms of the proton-bound dimer in the mass spectrometer ion source has two major consequences. The more important is the fact that the PAs of both isomers can be measured, as demonstrated in this paper. The measurement of PAs can in turn be used as a tool for probing structure, i.e. the PA of a given species indicates which form(s) of the isomer are present in the mass spectrometer. The second consequence of the existence of proton-bound dimers of two isomeric radicals is a limitation in the accuracy to which the PA of either isomer can be measured, especially the higher energy isomer. This is the result of a competition between the higher and lower energy isomers for proton-bound dimer formation with the reference compound in the chemical ionization source.

The results reported here demonstrate the applicability of the kinetic method to the accurate measurement of the PAs of free radicals. Extension of the kinetic method to the measurement of PAs of still other types of radical species appears promising. This study also illustrates the utility of *ab initio* calculations as an adjunct to experimental investigations.

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Supplementary Material Available: Listing of UHF/6-31G** optimized geometries for the radicals and radical cations whose energies are given in Table 4 (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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