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Protonated *p*-Benzoquinone

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The structure and energetics of protonated *p*-benzoquinone (pBQ) have been investigated using high-pressure mass spectrometry and ab initio calculations. The experimental proton affinity of pBQ is 801.4 ± 8.9 kJ/mol (191.5 ± 2.1 kcal/mol) (1σ) from bracketing measurements and hydration thermochemistry. This value is supported by theory and by analogies with related compounds. In its protonation chemistry, pBQ behaves as an aliphatic ketone, both structurally and energetically. The dissociation of the hydrate $(pBQH^+)\cdot(H_2O)$ is characterized by $\Delta H°_D = 90.0 \pm 2.3$ kJ/mol and $\Delta S°_D = 123.4 \pm 4.9$ J/mol·K (95% confidence).

Introduction

Quinones are an interesting and important class of organic compound whose chemistry is dominated by their electron-accepting character.[1,2] Well-known reactions include reduction to semiquinones and hydroquinones, applications in synthesis as oxidizing agents, facile Michael or conjugate addition with nucleophiles, and Diels−Alder condensation with electron-rich dienophiles. In this paper, we discuss rather different chemistry, in which the quinone serves as an electron donor. In particular, we have determined the structure and stability of protonated *p*-benzoquinone.

There is a very limited literature dealing with the reactivity of protonated quinones. The typical electrophilic reactions of quinones are facilitated by protonation. For example, the oxidizing power of quinones is enhanced by protonation in strongly acidic media,[3] and protonated intermediates have correspondingly been implicated in the reduction of quinones.[4,5] Much milder nucleophiles will react with quinones if the latter are protonated or otherwise O-electrophilically activated.[6] Likewise, Diels−Alder reactions of protonated benzoquinones are especially facile.[7] In the current study, we present the results of gas-phase experiments, ab initio calculations, and comparisons with other protonated and cationic species.

Experimental Details

Kinetic measurements were carried out with the NIST pulsed high-pressure mass spectrometer system using techniques described in detail previously.[8] Samples of *p*-benzoquinone (pBQ) were prepared by dissolving 10−20 mg of the solid in 2 mL of H_2O, followed by syringe-injection of the appropriate quantity into a 2.5 L gas introduction reservoir maintained at 180 °C and containing the other components. The bulk carrier gas was methane. Total ion source pressures were in the range 3−6 mbar, with pBQ and the other reference bases comprising a mole fraction of 10^{-4}−10^{-6} of the mixture. The hydration thermochemistry of $pBQH^+$ was investigated in mixtures containing mole fractions of H_2O between 0.010 and 0.096. Measurement conditions for acidic site diagnostics in $pBQH^+$ were 3 mbar of CH_4, 0.18 mbar of D_2O, and trace pBQ ($T = 500$ K).

Gas-phase experiments with pBQ are complicated by the low volatility of the compound (melting point = 114 °C). Our sample preparation and introduction systems were maintained at 150 °C, with higher source temperatures. Nonetheless, the possibility of partial condensation in undetected cool spots prohibited any confident assessment of the partial pressure of pBQ. This precluded quantitative studies of proton transfer equilibria. Instead, we carried out a series of bracketing measurements, in which the direction of reaction 1 is determined using several bases **B** with known proton affinities.

$$\mathbf{B}H^+ + pBQ \rightleftharpoons pBQH^+ + \mathbf{B} \qquad (1)$$

Typical conditions were a mole fraction of **B** of 2×10^{-5} to 4×10^{-5} and a nominal mole fraction of pBQ of 2×10^{-5} in CH_4 at a total source pressure of 6.5 mbar at 600 K.

Samples were ionized by 0.5 ms pulses of 1.5 keV electrons, and temporal ion profiles were monitored for 5−6 ms in order to ensure that constant ion ratios had been attained during the observation time for the hydration equilibrium reaction of interest. Uncertainties are standard uncertainties (1σ) unless otherwise indicated.

Computational Details

Preliminary calculations of the structure, vibrational frequencies, and energetics of selected species were done using the AM1 semiempirical model[9] as implemented in

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(1) Patai, S., Ed. *The Chemistry of Functional Groups: The Chemistry of the Quinonoid Compounds*; Wiley: New York, 1974; Parts 1 and 2.

(2) Patai, S., Rappoport, Z., Eds. *The Chemistry of Functional Groups: The Chemistry of the Quinonoid Compounds*; Wiley: New York, 1988; Vol. II, Parts 1 and 2.

(3) (a) Becker, H.-D. Reference 1, Chapter 7. (b) Becker, H.-D.; Turner, A. B., Reference 2, Chapter 23. (c) Chambers, J. Q. Reference 2, Chapter 12.

(4) Hammerich, O.; Parker, V. D. *Acta Chem. Scand.* **1982**, *B36*, 63.

(5) Gust, D.; Moore, T. A.; Moore, A. L.; Ma, X. C.; Nieman, R. A.; Seely, G. R.; Belford, R. E.; Lewis, J. E. *J. Phys. Chem.* **1991**, *95*, 4442.

(6) (a) Finley, K. T. Reference 1, Chapter 17. (b) Finley, K. T. Reference 2, Chapter 11.

(7) Lu, L.; Yang, S. S.; Wang, Z.; Cooks, R. G.; Eberlin, M. N. *J. Mass Spectrom.* **1995**, *30*, 581.

(8) Meot-Ner (Mautner), M.; Sieck, L. W. *J. Am. Chem. Soc.* **1991**, *113*, 4448.

(9) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

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the MOPAC[10] and Ampac[11] program packages.[12] AM1 input and initial MMX minimization were done using the PCmodel program.[12,13]

Ab initio molecular geometries and vibrational frequencies were determined at the Hartree–Fock (HF) level using the 6-31G* basis set. HF/6-31G* vibrational frequencies were scaled by 0.893. Vibrational zero-point energies (ZPEs) were taken as one-half the sums of the scaled frequencies. Electron correlation was included using frozen-core MP2/6-31G* and MP2/6-311G** single-point calculations. We consider the MP2/6-311G** proton affinity results to be the most reliable in the present study.

For comparison with the MP2//HF results, a series of density functional calculations was also performed using the hybrid, gradient-corrected B3LYP functional,[14] which is closely related to the functional that Becke optimized for accurate thermochemistry.[15] Geometries, vibrational frequencies (scaled by 0.96), and energetics were computed at the B3LYP/6-31G* level.

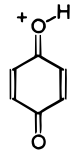
Singlet–triplet energy gaps in the phenoxyl cation (PhO^+) and in $pBQH^+$ ($HOPhO^+$) were computed at several levels of wavefunction-based and density-functional theory using the HF/6-31G* geometries and ZPEs. For PhO^+ the relevant states are $^1A_1$ and $^3A_2$, and for $HOPhO^+$ the relevant states are $^1A'$ and $^3A''$. For PhO^+, the active space for the CASSCF(8,8) calculations included the π-electrons and orbitals and the oxygen nonbonding orbital of b_2 symmetry. For $HOPhO^+$, the CASSCF(10,9) also included the π-pair on the hydroxyl oxygen atom. Static electron correlation is often very important in the computation of singlet–triplet gaps because the singlet states in molecules such as PhO^+ or CH_2 have two important configurations (σ^2 and π^2) for their nonbonding electrons. In the present calculations, the importance of electron correlation in PhO^+ and $HOPhO^+$ was evinced by (1) major contributions from several configurations in the CASSCF calculations and (2) large t_2 amplitudes in the coupled-cluster calculations. Perturbative methods such as MP2 are not expected to give reliable results for systems with such important near-degeneracy effects. In contrast, the CCSD(T) method includes most of the correlation energy and the density-functional calculations include electron correlation in a self-consistent way.

The Gaussian-92/DFT,[16] Gaussian-94,[17] ACES II,[18,19] and GAMESS[20] packages were used for the ab initio calculations.[12] Geometric stationary points were routinely characterized by vibrational analysis.

Auxiliary thermochemical data are from ref 21 unless otherwise noted. The ion convention is used in the present work and is indicated by the use of the symbol H instead of $H°$ for enthalpies.[21]

Results

Site of Protonation. As shown below, pBQ can be protonated either on oxygen or on carbon to yield **1** or **2**, respectively. Isomers **3** and **4** are the products of putative, successive isomerization reactions of **2**. The site of protonation was probed using a common mass-spectrometric diagnostic for counting the acidic hydrogens in gaseous cations.[22] In this procedure, a substantial concentration of D_2O is introduced into the ion source together with the base/CH_4 mixture. Isotope exchange, reaction 2, is then monitored in an otherwise unreactive environment. Thus, the number of acidic hydrogens is simply the m/z shift resulting from H–D exchange in RH_n^+ under conditions in which the reaction has gone to completion, that is, when all acidic protons have been exchanged for deuterons.



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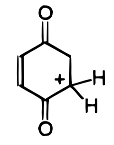

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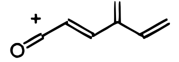

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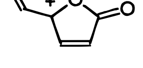

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$$RH_n{}^+ + mD_2O \rightarrow RH_{n-m}D_m{}^+ + mHDO \qquad (2)$$

Diagnostics were first tested with the carbon base toluene, which is known to undergo ring protonation.[22] As expected, it was found that m/z 93, $(C_6H_5CH_3)H^+$, was quantitatively converted to m/z 99, $(C_6D_5CH_3)D^+$, defining six interchangeable acidic hydrogen sites (five phenyl hydrogens plus the added proton). Under identical conditions, the terminal ion found in $pBQ/CH_4/D_2O$ mixtures was m/z 110, which is shifted only one unit from $pBQH^+$ (m/z 109). Protonation therefore occurs at the oxygen site. This technique is extremely sensitive toward competing structures, and even minor ring involvement would have been revealed. In support of the experimental conclusion that protonation occurs on oxy-

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[10] MOPAC Version 6.0: Stewart, J. J. P. QCPE program 455.

[11] Ampac 2.10: Dewar, M. J. S. Program 506, Quantum Chemistry Program Exchange, Bloomington, IN.

[12] Certain commercial materials and equipment are identified in this paper in order to specify procedures completely. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified is necesarily the best available for the purpose.

[13] PCmodel version 4.0: Serena Software, Bloomington, IN 47402.

[14] Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

[15] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

[16] Gaussian 92/DFT: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1993.

[17] Gaussian 94: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995.

[18] ACES II, an ab initio program system authored by J. F. Stanton, J. Gauss, J. D. Watts, W. J. Lauderdale, and R. J. Bartlett. The package also contains modified versions of the MOLECULE Gaussian integral program of J. Almlöf and P. R. Taylor, the ABACUS integral derivative program of T. U. Helgaker, H. J. A. Jense, P. Jorgensen, and P. R. Taylor, and the PROPS property integral package of P. R. Taylor.

[19] Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. *Int. J. Quant. Chem.* **1992**, *S26*, 879.

[20] Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

[21] Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

[22] Harrison, A. G. *Chemical Ionization Mass Spectrometry*; CRC Press: Boca Raton, FL, 1983; Chapter 9.

Table 1. Relative Energies of Isomers of Protonated *p*-Benzoquinone (pBQ), in kJ/mol[a,b]

isomer	AM1	HF/ 6-31G*	B3LYP/ 6-31G*	MP2/ 6-31G*	MP2/ 6-311G**
1	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)
2	158.8	181.8		191.1	200.5
3		72.3	73.6	65.9	60.8
4		−9.9	−9.3	−5.1	8.0

[a] 4.184 kJ = 1 kcal. [b] HF/6-31G* geometries and ZPEs are used for frozen-core MP2 energies. MP2/6-311G** is the most reliable. The B3LYP/6-31G* optimization for **2** failed to locate a nearby minimum (see text).

gen, the AM1 semiempirical calculation predicts **1** to be more stable than **2** by 159 kJ/mol (4.184 kJ/mol = 1 kcal/mol).

A competing process that is *irreversible*, however, could remain hidden. In particular, carbon protonation might lead to irreversible isomerization to **3** or **4**. Since **3** and **4** lack acidic protons, they cannot undergo H/D exchange. Quantum calculations can address this question.

Our initial ab initio calculations failed to identify structure **2** as a local minimum on the molecular potential energy surface. Instead, B3LYP/6-31G* optimization of **2** led to **3**, and HF/6-31G* optimization of **2** led eventually to **4** (via **3**). These interesting geometry optimizations suggest that protonation at carbon (**2**) does indeed lead irreversibly to **3** and possibly to **4** in the absence of stabilizing collisions. A subsequent attempt, using slightly different starting parameters, did locate a local HF/6-31G* minimum corresponding to structure **2**. The B3LYP/6-31G* results were unchanged. Calculated relative energies are summarized in Table 1 and indicate that protonation at carbon is about 200 kJ/mol less favorable than protonation at oxygen. For cationic olefin **3**, the *Z* isomer is unstable; both HF/6-31G* and B3LYP/6-31G* geometry optimizations lead to oxacycle **4**.

Proton-Bound Complex with Water. The energetics of the complex $(\mathrm{pBQH^+})\cdot(\mathrm{H_2O})$ was investigated because it can be combined with empirical correlations[23] to predict a value for PA(pBQ). The equilibrium reaction 3 was investigated over the temperature range 148−270 °C.

$$\mathrm{pBQH^+ + H_2O \rightleftharpoons (pBQH^+)\cdot(H_2O)} \tag{3}$$

Note that a knowledge of the absolute concentration of neutral pBQ is not required when studying association equilibria involving $\mathrm{pBQH^+}$ as the core ion; only the $\mathrm{H_2O}$ concentration needs to be established in this particular case. The resulting van't Hoff plot for the hydration reaction is given in Figure 1. For the dissociation of the proton-bound complex into $\mathrm{pBQH^+}$ and $\mathrm{H_2O}$, the derived bond energy and entropy change are $\Delta H^\circ_D = 90.0 \pm 2.3$ kJ/mol and $\Delta S^\circ_D = 123.4 \pm 4.9$ J/mol·K (95% confidence).

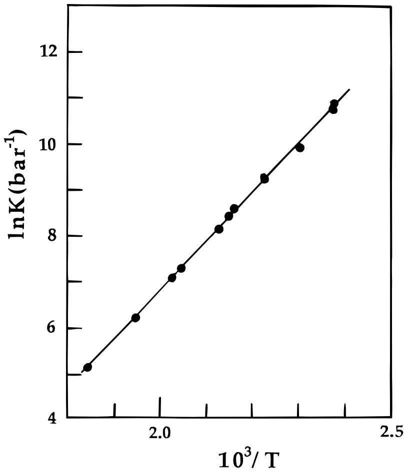

Figure 1.

We note that covalent formation of the Michael addition product in the reaction between $\mathrm{pBQH^+}$ and $\mathrm{H_2O}$,[24] resulting in protonated 2,4-cyclohexadienone-4,6-diol, can be ruled out under our measurement conditions for three reasons: (i) covalent insertions invariably yield ΔS°_D values in excess of 170 J/mol·K, which is inconsistent with the experimental value of 123.4 J/mol·K, (ii) loss of $\mathrm{H_2O}$ followed by rehydration of the product ion would exhibit overall steady-state kinetics rather than the equilibrium kinetics characteristic of an electrostatically-bonded association ion, and (iii) we calculate the hydrogen-bonded complex to be more stable than the Michael addition product by 128, 102, and 105 kJ/mol at the HF/6-31G*, frozen-core MP2//HF/6-31G*, and frozen-core MP2/6−311G**//HF/6-31G* levels, respectively, including corrections for zero-point vibrational energy.

For the thermochemical data obtained from the van't Hoff plot, the standard uncertainty arising from random effects is derived from the standard deviation of the slope (for ΔH°_D) and intercept (for ΔS°_D) in the least-squares fit to a linear regression analysis. The indicated uncertainties are these values multiplied by a coverage factor obtained from the *t*-distribution for a confidence level of 0.95, with $n - 2$ degrees of freedom, where n is the number of points included in the plot. An independent estimate of the uncertainty arising from both random and systematic effects is given by Meot-Ner and Sieck[8,25] and by Lias et al.,[26] and in replicate data sets for association reactions from various sources,[27] which suggests standard uncertainties of ±4 kJ/mol for ΔH°_D and ±8 J/mol·K for ΔS°_D.

Proton Affinity. The observed ordering of proton affinities (PAs) in the bracketing experiment was toluene < $\mathrm{CH_3OCH_3}$ < $\mathrm{C_2H_5CN}$ < pBQ < i-$\mathrm{C_4H_8}$ < acetone. The gas phase PA scale has been the subject of an exhaustive reexamination and evaluation at NIST,[28] and significant changes are required in many of the values recommended in the original 1984 compendium.[26] As of this writing, the new PA(600 K) values for the bracketing bases of interest here are PA($\mathrm{C_2H_5CN}$) = 797.5 and PA(i-$\mathrm{C_4H_8}$) = 804.6 kJ/mol. We therefore deduce that PA(pBQ) = 801.1 ± 3.6 kJ/mol at 600 K. The corresponding values at 300 K are PA($\mathrm{C_2H_5CN}$) = 794.1 and PA(i-$\mathrm{C_4H_8}$) = 802.9 kJ/mol, yielding PA(pBQ) = 798.5 ± 4.4 kJ/mol at 300 K. The entire reference PA scale is also subject to an additional standard uncertainty of ± 5.0 kJ/mol;[28] i.e., the whole scale is subject to an upward or downward shift of this magnitude without affecting the PA differences between various members of the scale. This additional uncertainty leads to a combined standard uncertainty of ±6.7 kJ/mol at 300 K for PA(pBQ) using the bracketing method.

As mentioned above, the strength of the ionic hydrogen bond in $(\mathrm{pBQH^+})\cdot(\mathrm{H_2O})$ can be used to estimate PA(pBQ)

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(23) Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1984**, *106*, 1257.

(24) Getek, T. A.; Vestal, M. L.; Vestal, C. H.; Korfmacher, W. A.; Miller, D. W.; Freeman, J. P. *Org. Mass Spectrom.* **1991**, *26*, 697.

(25) Meot-Ner (Mautner), M.; Sieck, L. W. *Int. J. Mass Spectrom. Ion Proc.* **1991**, *109*, 187.

(26) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

(27) Keesee, R. G.; Castleman, W. A. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1011.

(28) Hunter, E. P. Work in progress.

Table 2. Calculated and Experimental Proton Affinities (300 K) in kJ/mol[a,b]

method	pBQ	acetone	benzene
AM1	790.4 kJ/mol	803.4	763.4
HF/6-31G*	815.5	829.3	796.5
B3LYP/6-31G*	815.9	824.2	786.3
MP2/6-31G*	798.7	798.8	744.2
MP2/6-311G**	805.3	815.7	736.0
experiment	801.4 ± 8.9	817.6 ± 5.0[c]	744.8 ± 5.0[c]

[a] 4.184 kJ = 1 kcal. [b] Geometries and ZPEs are as in Table 1. MP2/6-311G** is the most reliable calculation. Experimental uncertainties are 1σ. [c] Reference 28.

by using empirical correlations developed for hydrogen bonds involving oxonium ions donors and oxygen-base acceptors ($OH^+\cdots O$ bonds). Such correlations are useful for predicting the proton affinity difference, $\Delta PA = PA(A) - PA(B)$, based upon the $(AH^+)\cdot B$ dissociation energy ΔH°_D. Plots of dissociation energy versus ΔPA reproducibly yield straight lines with slopes and intercepts characteristic of the functional groups in A and B. These correlations have proved especially useful for accurately assessing bond strengths and proton affinities in experimentally inaccessible systems that involve thermolabile or nonvolatile compounds, including many biomolecules.

The correlation for $OH^+\cdots O$ bonds has been formulated by Mautner[23] and has the form $\Delta H^\circ_D = 127.2\ (\pm 1.7) - 0.30(\Delta PA)$ kJ/mol. In this case, $\Delta PA = PA(pBQ) - PA(H_2O)$. Substituting the experimental ΔH°_D value of 90.0 kJ/mol yields $\Delta PA = 124.0 \pm 5.9$ kJ/mol. Taking $PA(H_2O) = 697$ kJ/mol[26] then gives $PA(pBQ) = 821.0 \pm 5.9$ kJ/mol. However, the proton affinity data used to construct the original correlation line were taken from the 1984 evaluation by Lias et al.[26] As discussed above, the proton affinity scale has been revised since that time. In this region of the scale, recommended values have decreased by about 16.7 kJ/mol, so that $PA(i\text{-}C_4H_8) = 819.6$ has been superseded by $PA(i\text{-}C_4H_8) = 802.9 \pm 5.0$ kJ/mol.[28] Hence, the values from the old correlation must be adjusted. This leads to $PA(pBQ) = 804.3 \pm 7.7$ kJ/mol (combined standard uncertainty).

Since the number of electron pairs is unchanged by addition of a proton, electron correlation is usually relatively unimportant in ab initio predictions of proton affinities.[29,30] The values of PA(pBQ) computed at a few levels of theory are listed in Table 2. These values are corrected to 300 K using the calculated rotational constants and scaled vibrational frequencies. For comparison, Table 2 also includes calculated and experimental values of PA(acetone) and PA(benzene), which were chosen to represent bases that are protonated on oxygen and on carbon, respectively. The calculated entropies for the protonation reaction at 298 K, $S^\circ_{298}(BH^+) - S^\circ_{298}(B) - S^\circ_{298}(H^+)$, are −104.1, −76.8, and −94.5 J/mol·K for acetone, benzene, and pBQ, respectively.

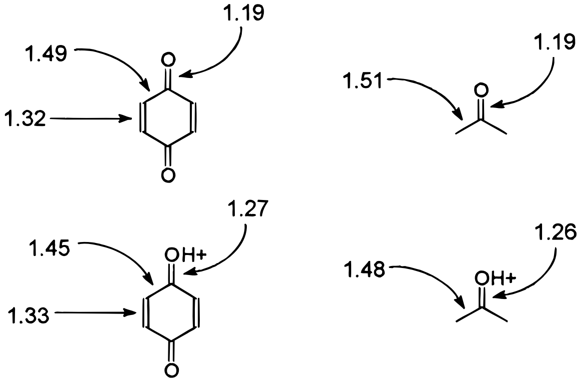
Due to cancellation of systematic errors, the calculated proton affinity difference, $PA(pBQ) - PA(acetone) = -10.4$ kJ/mol, is expected to be more accurate than the calculated absolute PA. We expect this difference to be uncertain by about 10 kJ/mol. Using the experimental[28] value $PA(acetone) = 817.6 \pm 5.0$ kJ/mol and the frozen-core MP2/6-311G**//HF/6-31G* energetics, we obtain a corrected value $PA(pBQ) = 807.2 \pm 11.2$ kJ/mol, which is our best theoretical value.

The geometry and vibrational frequencies of pBQ have been computed before, using the HF/3-21G,[31] UNO-CAS-(8,8)/4-21G,[32] and MP2/6-31G*[33] methods. However, they are calculated here for consistency with our HF/6-31G* calculations. HF/6-31G* geometries of acetone and pBQ in both neutral and protonated forms are indicated below.

Table 3. Singlet-Triplet Energy Gaps (in kJ/mol[a]) for Phenoxyl Cation (PhO^+) and for Protonated *p*-Benzoquinone ($pBQH^+$)[b]

	basis set PhO^+		basis set $pBQH^+$	
calculation	6-31G*	6-311G**	6-31G*	6-311G**
HF	−34		36	
MP2	144	145	148	152
PMP2	100	101	134	137
CASSCF	85	120	180	
CCSD(T)	71	73	120	125
B3LYP	53	57	94	99

[a] 4.184 kJ = 1 kcal. [b] Geometries and ZPEs were computed at the HF/6-31G* level.



The keto moieties in the two molecules are very similar, as are the geometric changes upon protonation. The B3LYP/6-31G* results are very similar and do not merit separate discussion. For all the quinone-derived molecules in this study, computed vibrational spectra, detailed geometries, and total energies are tabulated in the supporting information, which is available separately.

Singlet−Triplet Gap. The singlet−triplet gap in the phenoxyl cation, PhO^+, has been reported to be 83 kJ/mol based upon a photoelectron spectrum of the PhO radical.[34] Since $pBQH^+$ is alternatively named *p*-hydroxyphenoxyl cation, $HOPhO^+$, its singlet−triplet gap is expected to be amenable to the same theoretical treatments that provide reasonable results for PhO^+. Using RHF/6-31G* geometries and ZPEs for singlet states and UHF/6-31G* geometries and ZPEs for triplet states, we obtain the adiabatic excitation energies listed in Table 3. For PhO^+, the CASSCF results do not appear to have converged with respect to the one-electron basis set. In contrast, the CCSD(T) results appear converged with respect to basis set for both PhO^+ and $HOPhO^+$. We therefore favor the CCSD(T)/6-311G**//HF/6-31G* values, which are 73 kJ/mol for PhO^+ and 125 kJ/mol for $HOPhO^+$. We note that the density-functional calculations give systematically lower, but reasonable, values and also appear converged with respect to basis set.

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(29) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(30) Del Bene, J. E. *J. Comput. Chem.* **1985**, *6*, 296.

(31) Chipman, D. M.; Prebenda, M. F. *J. Phys. Chem.* **1986**, *90*, 5557.

(32) Liu, R.; Zhou, X.; Pulay, P. *J. Phys. Chem.* **1992**, *96*, 4255.

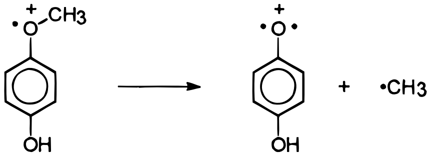
(33) Yamakita, Y.; Tasumi, M. *J. Phys. Chem.* **1995**, *99*, 8524.

(34) Dewar, M. J. S.; David, D. E. *J. Am. Chem. Soc.* **1980**, *102*, 7387.

Discussion

The experimental proton affinities obtained in this study are PA(pBQ) = 798.5 ± 6.7 kJ/mol from bracketing and PA(pBQ) = 804.3 ± 7.7 kJ/mol from the correlation with hydration energy (standard uncertainties). Weighting the two methods equally gives a final experimental value at 300 K of PA(pBQ) = 801.4 ± 8.9 kJ/mol. This is corroborated by our best theoretical estimate of PA(pBQ) = 807 ± 11 at 300 K, based upon ab initio energetics and the experimental proton affinity of acetone.

The experimental proton affinity, combined with $\Delta_f H_{298}(H^+) = 1530.0 \pm 0.1$ and $\Delta_f H^\circ_{298}(\text{pBQ}) = -123 \pm 4$ kJ/mol,[21] leads to an enthalpy of formation $\Delta_f H_{298}(\text{pBQH}^+) = 605.6 \pm 9.8$ kJ/mol. This is much lower than the recent value of 678 kJ/mol derived from the ion's appearance energy, AE = 11.03 eV, in the electron impact mass spectrum of *p*-hydroxyanisole.[35] Since this experiment is in agreement with earlier values, AE(pBQH$^+$/*p*-HOC$_6$H$_4$OCH$_3$) = 11.10 ± 0.1 eV[36] and 11.01 ± 0.1 eV,[37] the measurement appears reliable. However, thermochemistry derived from appearance energies can be problematic. One common problem is that the internal energy of the fragments is unknown. In particular, it is likely that homolytic and least-motion O−CH$_3$ bond cleavage in the cation radical *p*-HOC$_6$H$_4$OCH$_3{}^+$ would generate the pBQH$^+$ ion in its triplet state, not its ground singlet state, since there is no least-motion pathway that leads to the singlet (see below). If this is correct, then the triplet state of pBQH$^+$ lies about 72 kJ/mol above the ground state.



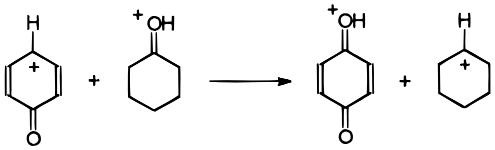
For comparison, the singlet−triplet gap in the (unhydroxylated) phenoxyl cation has been reported to be 83 kJ/mol,[34] and our CCSD(T) calculations suggest that the singlet−triplet gap in pBQH$^+$ is about 125 kJ/mol. This is greater than the singlet−triplet gap in unsubstituted PhO$^+$ because the *p*-hydroxyl group is a π-donor and stabilizes the singlet state more than the triplet.

Comparisons with related molecules support our measured value for PA(pBQ). The geometries illustrated above indicate that pBQ shows negligible aromatic character in its protonation reaction. This suggests that analogies with ordinary, aliphatic ketones will be valid. For example, a correlation has been observed between ionization potentials and proton affinities (eq 4). The

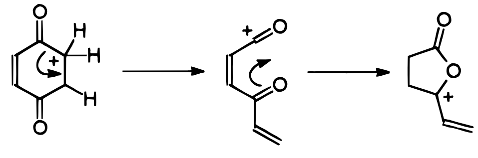
$$\text{PA(M)} = C + K\cdot\text{IP(M)} \qquad (4)$$

values of the constants C and K are characteristic for a given class of molecule. For ketones, $C = 1188$ kJ/mol and $K = -0.39$.[21] Since IP(pBQ) = 10.04 ± 0.18 eV, the correlation yields PA(pBQ) = 812 ± 19 kJ/mol. Adjusting for the revisions in the proton affinity scale (see Results) leads to PA(pBQ) = 795 ± 19 kJ/mol, in good agreement with our measured value of 801.4 ± 8.9 kJ/mol.

We can also estimate the enthalpy of formation of pBQH$^+$ by approximating the isodesmic reaction shown below as thermoneutral. This leads to $\Delta_f H_{298}(\text{pBQH}^+) \approx 602.5$ kJ/mol, in good agreement with our value of 605.6 ± 9.8 kJ/mol.



Scheme 1



2 **3** **4**

All the evidence indicates that an oxygen atom is the site of protonation in pBQH$^+$. It is indicated by our ab initio calculations, and the good agreement between the calculated and measured proton affinities suggests that the calculations are correct. The consistency with empirical correlations for OH$^+\cdots$O bonds also supports O-protonation.

It is likely that protonation of pBQ at carbon will lead to ring opening to acylium ion **3** and possibly to subsequent formation of the conjugated cationic lactone **4** (Scheme 1). If **2** does rearrange spontaneously and irreversibly, then the success of the proton affinity bracketing experiment indicates that ring-protonation is insignificant. From the energetics in Tables 1 and 2, we estimate that the effective proton affinity at carbon is 600 kJ/mol. Thus, proton donors with proton affinities less than 600 kJ/mol could protonate at carbon. In particular, methane is a common reagent for chemical ionization in mass spectrometry. PA(CH$_4$) = 540 kJ/mol,[28] so protonation at carbon is energetically accessible from CH$_5{}^+$. Thus, the rearrangements depicted in Scheme 1 could be tested by following low-pressure chemical ionization with a structural probe such as ion-molecule reactions or collisional dissociation.

Conclusions

Gas-phase protonation of *p*-benzoquinone occurs on oxygen; ring protonation is about 200 kJ/mol less favorable. The proton affinity of pBQ is 801.4 ± 8.9 kJ/mol (1σ). This experimental value is supported by ab initio calculations and by empirical correlations involving similar compounds. The correlations and quantum chemical calculations also indicate that pBQ behaves as an aliphatic ketone in the protonation reaction. Finally, the calculations indicate that if a strong acid did protonate pBQ on the ring, the product would probably rearrange by ring opening and subsequent closure to a cationic lactone (**2** → **3** → **4**).

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Supporting Information Available: Tables S1−S21, giving geometries, vibrational spectra, and total energies (15 pages). This material is contained in 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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(35) Ponomarev, D. A.; Takhistov, V. V.; Misharev, A. D.; Orlov, V. M. *Russ. J. Gen. Chem.* **1994**, *64*, 908.

(36) Brown, P. *Org. Mass Spectrom.* **1970**, *4*, 519.

(37) Tait, J. M. S.; Shannon, T. W.; Harrison, A. G. *J. Am. Chem. Soc.* **1962**, *84*, 4.