

Thermodynamics of Disproportionation and Heats of Hydration of 1,4-Benzosemiquinone and 1,4-Naphthosemiquinone at pH 7.1

Antonio E. Alegria,* Carlos Muñoz,[†] and Maria S. Rodriguez[†]

Department of Chemistry, CUH Station, University of Puerto Rico, Humacao, Puerto Rico 00661
(Received: May 3, 1989)

The thermodynamics of disproportionation of 1,4-benzosemiquinone (BQ^{•-}) and 1,4-naphthosemiquinone (NQ^{•-}) in cacodylic-cacodylate buffer at pH 7.1 was studied by electron spin resonance (ESR) spectroscopy and solution calorimetry. The disproportionation of BQ^{•-} was found to be more exergonic and exothermic than that corresponding to NQ^{•-} in both aqueous and gas phases. These semiquinones disproportionate about 40 times more exothermically in the gaseous than in the aqueous phase. The differences between the enthalpies of disproportionation corresponding to BQ^{•-} and NQ^{•-} are 51 and 14 kJ/mol in the gaseous and aqueous phases, respectively. The heats of hydration of BQ^{•-} and NQ^{•-} were determined with a convenient thermochemical cycle based on the enthalpies of disproportionation. The single-ion heats of hydration of BQ^{•-} and NQ^{•-} were found to be -360 and -377 kJ/mol, respectively. The heats of hydration of the net negative charge in BQ^{•-} and NQ^{•-} were found to be the same.

Introduction

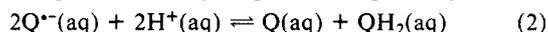
Semiquinones are important intermediates in electron-transfer processes occurring in biological respiratory processes^{1,2} and in antitumor and cytotoxic activities.³ Their role in photosynthesis⁴ and artificial solar energy conversion⁵ is also well documented. In biological systems, a common feature of the majority of these processes is the existence of an aqueous environment.

The participation of semiquinones in electron-transfer events is facilitated by the low redox potentials of the corresponding quinones,⁶ which are very dependent upon the type of environment in which the semiquinone is immersed and their internal structures.^{6,7} Redox potentials are strongly affected by the solution electron affinity of the oxidant that is essentially the summation of the gas-phase electron affinity of the oxidant and the heat of solvation of the reduced species. Knowledge of both the quinone gas-phase electron affinities and the heats of hydration of the corresponding semiquinones should aid in understanding the role of semiquinones in the electron-transfer processes in which they are involved, especially for the more hydrophylic ones.

The important role of ion solvation in controlling the stabilities of organic anions has been demonstrated by the classical work of Brauman and Blair⁸ and by Jordan and co-workers⁹ where relative stabilities of organic ions in the gas phase are opposed compared to the corresponding ones in solution. The extensive measurements of the heats of solution of organic anion radical salts performed by Stevenson and co-workers as a function of solvents and counterion have contributed to the understanding of the interrelated roles of anion structure, counterion, and solvent in the solvation process of these salts.¹⁰⁻¹² These have been based on solution calorimetric measurements of the reaction of π anions with either water or iodine. The heats of solvation of sodium salts of semiquinones in hexamethylphosphoramide (HMPA) have also been determined in a similar manner in our laboratory.¹⁶ However, no heats of hydration of organic π anion radicals have been previously determined, due to the low stability of these species in water. In this work, we have found that 1,4-benzosemiquinone (BQ^{•-}) and 1,4-naphthosemiquinone (NQ^{•-}) are stable enough in buffered (pH 7.1) aqueous solutions to permit the determination of their corresponding heats of hydration, eq 1. This was ac-



complished by measuring the corresponding heats of disproportionation at pH 7.1, eq 2, where Q^{•-}, Q, and QH₂ are the semiquinone, quinone, and hydroquinone, respectively.



Both of the semiquinones included in this work are anions at pH 7.1. At this pH value, the ratio of the concentration of the

anion to the corresponding protonated species (HQ[•]) is about 10³/1. This ratio can be calculated from the corresponding pK_a values of the protonated semiquinones.¹³ Only the diprotonated hydroquinone species are present at this pH for both BQH₂ and NQH₂ since the corresponding pK_a values are 9.9 and 9.3, respectively.¹⁴

Experimental Section

Materials. The compounds 1,4-benzoquinone (BQ), 1,4-naphthoquinone (NQ), hydroquinone (BQH₂), and 1,4-naphthalenediol (NQH₂) were purchased from Aldrich and purified by either sublimation or recrystallization from ethanol/water mixtures. Fresh stock solutions of these compounds were prepared in deionized water and used the same day. NQH₂ solutions were prepared in argon-saturated water and transferred only to argon-saturated solutions in order to avoid oxidation of the hydroquinone.

Cacodylic acid was purchased from Sigma Chemical, and a stock 520 mM solution (pH 7.4) was prepared by addition of NaOH(ac).

Disproportionation Constant. A similar system as that described by Evans¹⁵ was utilized for the semiquinone generation, i.e., an "H"-type pyrex cell connected to an ESR quartz flat cell (60 × 10 × 0.25 mm). In a typical experiment, an aliquot of the quinone stock solution was introduced through a septum into one side of the H cell. Another aliquot of the corresponding stock hydroquinone solution was added into the other side of the cell followed by the addition of buffer solution. Both solutions were

(1) Morton, R. A. *Biochemistry of Quinones*; Academic Press: New York, 1965.

(2) Crane, F. L. In *Biological Oxidations*; Singer, T. P., Ed.; Interscience: New York, 1968; p 533.

(3) For a recent review on this topic see: Powis, G. *Free Radical Biol. Med.* **1989**, *6*, 63.

(4) Clayton, R. K. *Photosynthesis: Physical Mechanisms and Chemical Patterns*; Cambridge University Press: London, 1980.

(5) Fendler, J. H. *J. Phys. Chem.* **1985**, *89*, 2730.

(6) Chambers, J. Q. In *The Chemistry of Quinonoid Compounds*; Patai, S., Ed.; Wiley: New York, 1974; Part 2, pp 737-791.

(7) Jaworski, J. S.; Lesnievska, E.; Kalinowski, M. K. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *105*, 329.

(8) Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc.* **1970**, *92*, 5986.

(9) Jordan, K. D.; Michejda, J. A.; Burrow, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 1295.

(10) Stevenson, G. R.; Schock, L. E.; Reiter, R. C. *J. Phys. Chem.* **1983**, *87*, 4004.

(11) Stevenson, G. R.; Hashim, R. T. *J. Am. Chem. Soc.* **1985**, *107*, 5794.

(12) Stevenson, G. R.; Hashim, R. T. *J. Phys. Chem.* **1986**, *90*, 3217.

(13) Willson, R. L. *Trans. Faraday Soc.* **1971**, *67*, 3020.

(14) Bailey, S. I.; Ritchie, I. M. *Electrochim. Acta* **1985**, *30*, 3.

(15) Evans, C. A. *Aldrichimica Acta* **1979**, *12*, 23.

[†] NIH-MBRS Student Participant.

purged gently with argon, with steps taken to carefully avoid mixing them. For this purpose, the argon was passed through a water tower before entering the sample solutions to avoid water loss in the samples. After 20 min of bubbling argon, the quinone and hydroquinone solutions were mixed and the resulting solution was also purged with argon for an additional 15 min. This solution was then transferred to an ESR flat cell and analyzed by ESR.

The overmodulated first derivative ESR spectrum corresponding to NQ^{•-} or the central line of that corresponding to BQ^{•-} were double integrated and this area compared to that corresponding to a spin standard of either tetramethyl-1-piperidinyloxy (TEMPO) or 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy (CTPO) dissolved in buffer. An X-band Bruker ER-200D ESR spectrometer coupled to an IBM CS-9000 computer was used for this purpose. The disproportionation constants (K_2) were obtained by subtracting half the semiquinone concentration, $[Q^{\bullet-}]$, from both the initial quinone, $[Q]_0$, and hydroquinone, $[QH_2]_0$, concentrations, eq 3.

$$K_2 = \{([QH_2]_0 - [Q^{\bullet-}]/2) ([Q]_0 - [Q^{\bullet-}]/2)\} / [H^+]^2 [Q^{\bullet-}]^2 \quad (3)$$

The pH remained constant at 7.1 during and after the disproportionation reaction.

Heats of Disproportionation. A similar H-cell setup as that described before was used with a Wilmad low-temperature aqueous solution sample cell. The temperature was varied and controlled with a Bruker ER 4111 VT temperature controller. The semiquinone concentration was determined as explained before with a spin standard solution placed in the same ESR quartz cell. At least three determinations of K_2 were made at each temperature. The heats of disproportionation were determined from Van't Hoff plots with use of the average values of K_2 at each temperature.

Heats of Solution. The heats of solution of BQ and BQH₂ were determined by dissolving known amounts of these compounds in 100.00 mL of 12.5 mM cacodylic-cacodylate buffer with use of solution calorimetry as described elsewhere.¹⁶ The calorimeter heat capacity, with water as the solvent, 515 J/°C, has been previously determined,¹⁶ and this value was used in the calorimetric measurements performed in this work. Four determinations corresponding to each compound were made.

Due to the low solubility of NQ and NQH₂ in water (2×10^{-5} and 3×10^{-3} M, respectively), their heats of solution in the aqueous buffer were estimated by measuring the change in temperature per mole of quinone or hydroquinone ($\Delta T/n$) occurring upon dissolving known amounts of these compounds in mixtures of acetone and 12.5 mM cacodylic-cacodylate buffer and extrapolating to 100% buffer, Figure 3.

Heat of Combustion of NQH₂. This was measured by bomb calorimetry using a Parr adiabatic calorimeter coupled to a thermistor and recorder as described elsewhere.¹⁷ The isochoric heat (ΔU°) obtained from the bomb calorimetry experiments was converted to the enthalpy of reaction (ΔH°) by $\Delta H^\circ = \Delta U^\circ + (\Delta n)RT$, where Δn is the difference between the number of moles of gaseous products and reactants involved in the combustion of 1 mol of NQH₂. In this case, $\Delta n = -1$. Three determinations were made.

Heat of Sublimation of NQH₂. The procedure used by Mackle and co-workers,¹⁸ where heats of sublimation were determined with gas chromatography, was adapted to this work. A 50-mL round-bottom flask, stoppered with a septum and containing 2 g of NQH₂ and a teflon coated stirring bar, was deaerated with argon and equilibrated to the atmospheric pressure with an oil bubbler. The closed system was then heated with an oil bath to

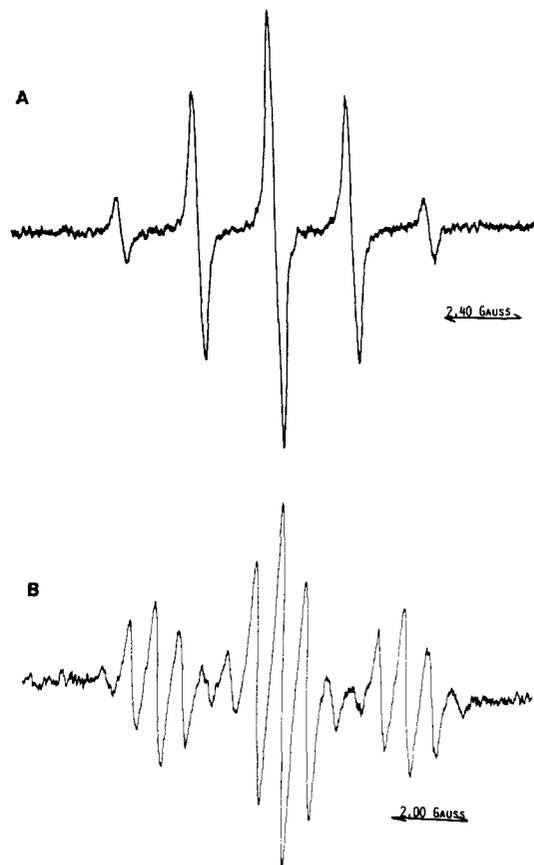


Figure 1. ESR spectra corresponding to (A) BQ^{•-} with a hyperfine coupling constant a_H (4H's) = 2.38 G and (B) NQ^{•-} with hyperfine coupling constants a_H (2H's) = 3.20 G and a_H (4H's) = 0.64 G in argon-saturated 12.5 mM cacodylic-cacodylate buffer, pH 7.1, in the presence of the corresponding quinone and hydroquinone.

a desired temperature that was controlled by a nichrome wire connected to a voltage transformer. After 20 min of equilibration at a given temperature, an 8.0-mL sample of the vapor above the solid was extracted with a gas-tight syringe and the syringe closed. A 2-mL amount of HPLC-grade acetonitrile was then drawn into the syringe avoiding entrance of ambient air. The syringe was closed again and the acetonitrile shaken with the vapor in order to dissolve all the NQH₂. This solution was partially poured out, and more fresh acetonitrile was introduced into the syringe and mixed with the extracted vapor. The absorbance of the resulting solution was measured at 244 nm. It was found, after correcting for dilution, that no more than the original 2 mL of acetonitrile was needed to completely dissolve all of the NQH₂ vapor. Since the absorbance of this solution is directly proportional to the gas phase concentration of NQH₂, then the NQH₂ partial pressure should be directly proportional to the product of the absorbance and the absolute temperature. Therefore, a plot of $\ln AT$ vs $10^3/RT$, where A is the absorbance corrected for dilutions, should be linear, and the heat of sublimation can be obtained from its slope. A value of 62 ± 4 kJ/mol was obtained for the heat of sublimation of BQ in this manner, which is in excellent agreement with that reported in the literature, i.e., 63 ± 3 kJ/mol,²¹ demonstrating the reliability of this technique.

Results and Discussion

When the argon-saturated quinone and hydroquinone buffer solutions are mixed, the corresponding semiquinone is produced at pH 7.1 as detected by ESR spectroscopy, Figure 1. These semiquinone solutions are stable for months under anaerobic and dark conditions. The semiquinone concentration, and thus the disproportionation constants, were obtained from the double in-

(16) Alegria, A. E.; Medina, A. N.; Tirado, R.; Soto, F. *J. Phys. Chem.* **1986**, *90*, 5333.

(17) Shoemaker, D. P.; Garland, C. W.; Steinfeld, J. I. *Experiments in Physical Chemistry*; McGraw-Hill: New York, 1974.

(18) Mackle, H.; Mayrick, R. G.; Rooney, J. J. *Trans. Faraday Soc.* **1960**, *56*, 115.

(19) Ilan, Y. A.; Czapski, G.; Meisel, D. *Biochim. Biophys. Acta* **1976**, *430*, 209.

(20) Patel, K. B.; Willson, R. L. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 814.

(21) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.

TABLE I: Thermodynamic Parameters Controlling the Disproportionation Equilibria of BQ^{•-} and NQ^{•-} at pH 7.1^a

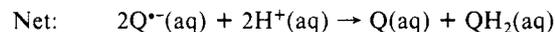
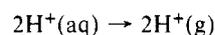
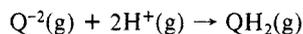
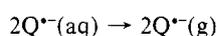
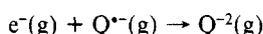
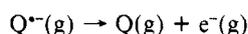
Q ^{•-}	K ₂	ΔG°/ (kJ mol ⁻¹)	ΔH°/ (kJ mol ⁻¹)	ΔS°/ (J mol ⁻¹ K ⁻¹)
BQ ^{•-}	(8.1 ± 1.2) × 10 ²⁰	-119 ± 1	-72.2 ± 0.3	158 ± 3
NQ ^{•-}	(3.1 ± 1.5) × 10 ¹⁸	-105 ± 1	-58 ± 2	159 ± 7

^a 25 °C. Buffer used: cacodylic-sodium cacodylate, 12.5 mM.

tegration of these spectra as described in the Experimental Section. A larger disproportionation constant at 298 K was obtained for BQ^{•-}, K₂ = (8.1 ± 1.2) × 10²⁰, than for NQ^{•-}, K₂ = (3.1 ± 1.5) × 10¹⁸. The disproportionation constant determined here for BQ^{•-} is of the same order of magnitude as that calculated from the data reported by Czapski and co-workers (4.2 × 10²⁰) obtained by pulse radiolysis.¹⁹

The heats of disproportionation were obtained from plots of ln K₂ vs 10³/RT, Figure 2, which yielded values of -72.2 ± 0.3 and -58 ± 2 kJ/mol for the disproportionation of BQ^{•-} and NQ^{•-}, respectively. Therefore, a more exothermic disproportionation for BQ^{•-} than that corresponding to NQ^{•-} is observed, in agreement with the relative magnitudes of the corresponding disproportionation constants. The thermodynamic parameters controlling the disproportionation reactions are summarized in Table I. A standard 2-electron-2-proton reduction potential larger for BQ (0.29 V vs SCE) than for NQ (0.07 V vs SCE)¹⁹ in aqueous solutions also correlates well with a greater tendency of BQ^{•-} to form its hydroquinone than NQ^{•-}.

Both enthalpy and entropy changes favor the spontaneous disproportionation of each semiquinone, although the differences in K₂ are mainly due to the differences in the enthalpies of disproportionation, Table I. This difference in disproportionation enthalpies should result from differences in the first and second gas-phase electron affinities of the corresponding quinone, the gas-phase heats of protonation of the corresponding quinone dianions, and the heats of hydration of the corresponding quinones and semi- and hydroquinones, Scheme I. In order to establish which of these factors explain this difference in heats of disproportionation, we first determined the heats of hydration corresponding to each of these species.

SCHEME I

In order to complete a thermochemical cycle where the heats of hydration of the semiquinones can be obtained, the enthalpies of solution of BQ, NQ, BQH₂, and NQH₂ were determined as described in the Experimental Section. The enthalpies of solution in 12.5 mM cacodylic-sodium cacodylate buffer of BQ and BQH₂ are +17 ± 3 and +18.4 ± 0.6 kJ/mol, respectively. Plots of ΔT/n vs the volume percent of acetone were used to estimate the heats of solution in 12.5 mM buffers of NQ(s) and NQH₂(s) as described above, Figure 3. These estimates were obtained by extrapolation of the linear portion of these graphs to 100% buffer by volume. The estimates obtained in this manner for the enthalpies of solution of NQ and NQH₂ in 12.5 mM buffer are 4 ± 2 and 22 ± 1 kJ/mol, respectively.

If the heats of disproportionation and the heats of solution described above are used together with other appropriate enthalpies found in the literature, the heats of hydration of the corresponding semiquinone plus that of the proton are obtained, Table II. The

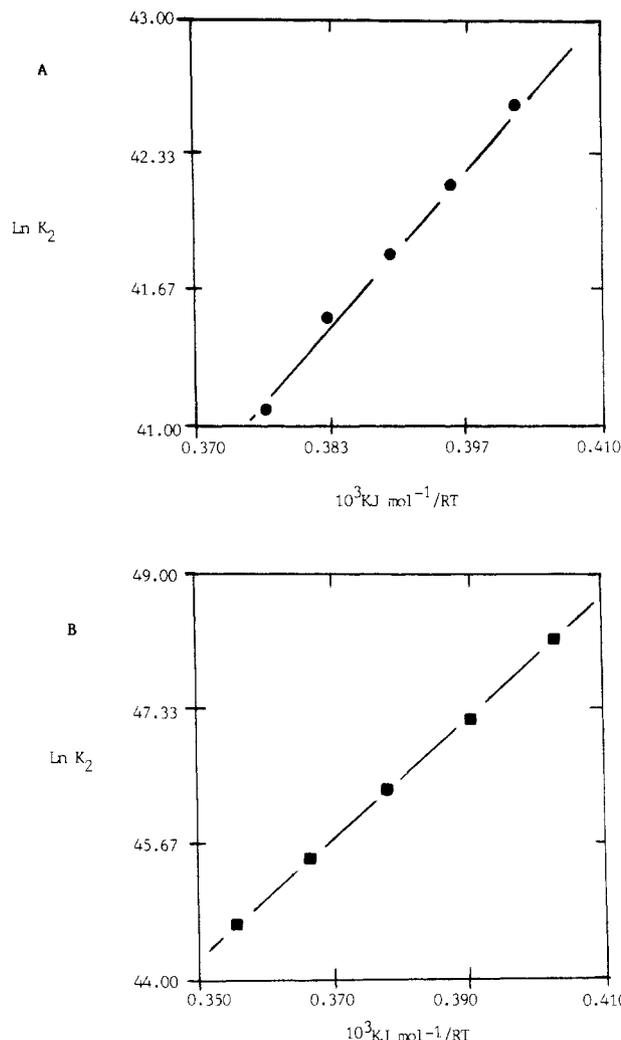


Figure 2. Graphs utilized in the determination of the enthalpies of disproportionation of (A) NQ^{•-} and (B) BQ^{•-} in 12.5 mM cacodylic-cacodylate buffer, pH 7.1.

heats of hydrogenation of both BQ and NQ were needed in this cycle to evaluate the corresponding heats of hydration, eq 4. These



were obtained by subtracting the heat of combustion of the corresponding hydroquinone from the summation of the enthalpies of combustion of the quinone and hydrogen. The heats of combustion of BQ(s) (-2725.3 ± 0.8 kJ/mol),²¹ BQH₂(s)²¹ (-2824.2 ± 1.1 kJ/mol), and H₂(g) (-285.76 ± 0.01 kJ/mol)²² are all available in the literature. The heat of combustion of NQ(s) (-4608.0 ± 1.8 kJ/mol)²⁰ is also available. However, to our best knowledge, the heat of combustion of NQH₂ has not been previously determined. The latter was determined in this work as described in the Experimental Section, yielding an average value of -4739 ± 7 kJ/mol. The values obtained for the heats of hydrogenation of BQ and NQ are shown in Table II.

The heats of hydration of the semiquinone-proton pairs can be calculated from the cycle in Table II as -1451 ± 8 and -1468 ± 12 kJ/mol for BQ^{•-} and NQ^{•-}, respectively. These values suggest that there is an increase in the exothermicity of the hy-

(22) Weast, R. C., Astle, M. J., Beyer, W. H., Eds. *CRC Handbook of Chemistry and Physics*, 66th ed.; CRC: Boca Raton, FL, 1986; p D-69.

(23) (a) Cooper, C. D.; Naft, W. T.; Compton, R. N. *J. Chem. Phys.* **1975**, *63*, 2752. (b) NQ gaseous electron affinity was calculated from the relative electron affinity reported by: Fukuda, E. K.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 2291. The electron affinity for gaseous BQ was reported in ref 23a.

(24) Weast, R. C., Astle, M. J., Beyer, W. H., Eds. *CRC Handbook of Chemistry and Physics*, 66th ed.; CRC: Boca Raton, FL, 1986; p F-184.

(25) Reference 24; p E-74.

TABLE II: Thermochemical Cycle Used in the Determination of the Heat of Hydration of Q^{•-} + H⁺ and the Single-Ion Heat of Hydration of Q^{•-} in 12.5 mM Cacodylic-Cacodylate Buffer, pH 7.1

reaction	$\Delta H^\circ_a / (\text{kJ mol}^{-1})$		ref
	BQ	NQ	
$\text{QH}_2(\text{aq}) + \text{Q}(\text{aq}) \rightarrow 2\text{Q}^{\bullet-}(\text{aq}) + 2\text{H}^+(\text{aq})$	+72.2 ± 0.3	+58 ± 2	this work
$\text{Q}(\text{s}) \rightarrow \text{Q}(\text{aq})$	+17 ± 3	+4 ± 2	this work
$2\text{Q}(\text{g}) \rightarrow 2\text{Q}(\text{s})$	-126 ± 6	-145 ± 8	21
$2\text{Q}^{\bullet-}(\text{g}) \rightarrow 2\text{Q}(\text{g}) + 2\text{e}^-(\text{g})$	+364 ± 2	+341 ± 2	23
$\text{QH}_2(\text{s}) \rightarrow \text{QH}_2(\text{aq})$	+18.4 ± 0.6	+22 ± 1	this work
$\text{Q}(\text{s}) + \text{H}_2(\text{g}) \rightarrow \text{QH}_2(\text{s})$	-187 ± 3	-155 ± 8	b
$2\text{H}^+(\text{g}) \rightarrow \text{H}_2(\text{s})$	-435.78 ± 0.01	-435.78 ± 0.01	24
$2\text{H}^+(\text{g}) + 2\text{e}^-(\text{g}) \rightarrow 2\text{H}^+(\text{aq})$	-2624.0 ± 0.1	-2624.0 ± 0.1	25
$2\text{H}^+(\text{g}) + 2\text{Q}^{\bullet-}(\text{aq}) + 2\text{H}^+(\text{aq})$	-2901 ± 15	-2935 ± 23	
$2\text{H}^+(\text{aq}) \rightarrow 2\text{H}^+(\text{g})$	+2182 ± 21	+2181 ± 21	26
$2\text{Q}^{\bullet-}(\text{g}) \rightarrow 2\text{Q}^{\bullet-}(\text{aq})$	-719 ± 36	-753 ± 44	

^aThe errors are those reported in the reference or estimated as the unit in the uncertain figure of the reported value. ^bFor Q = BQ, this enthalpy is obtained from the reported heats of combustion of BQ,²¹ BQH₂,²¹ and H₂.²² For Q = NQ, this enthalpy is obtained from the reported heats of combustion of NQ²¹ and H₂²² and that obtained for NQH₂ in this work. See the text.

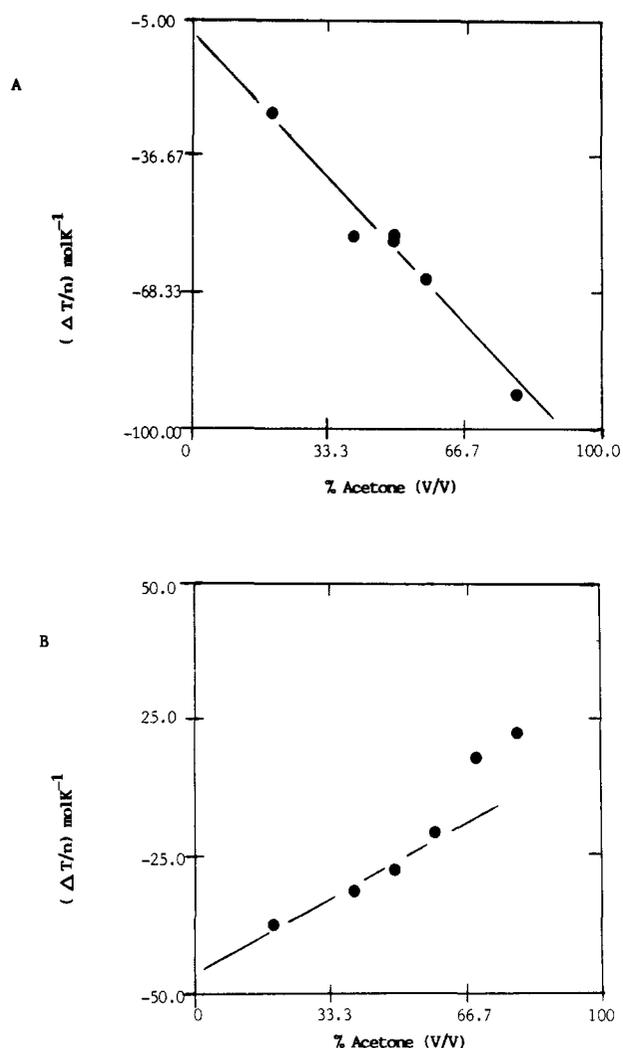


Figure 3. Estimation of the heats of hydration of (A) NQ(s) and (B) NQH₂(s) by extrapolation to 100% aqueous buffer by volume by plotting the temperature change per mole of dissolved solid against the volume percent of acetone. The intercepts are (A) -7 and (B) -44 °C/mol.

dration process upon extending the π cloud in the semiquinone system. An increase in the exothermicity of solvation has been observed upon increasing the π cloud size in polyacene radical anions in THF¹⁰ and semiquinones in hexamethylphosphoramide (HMPA).¹⁶

The enthalpies of hydration of BQ^{•-} and NQ^{•-} plus the proton obtained in this work are larger in magnitude than the heats of solution reported for polyacene radical ion-sodium ion pairs in

THF¹⁰ (-719 to -800 kJ/mol) or those reported for semiquinone sodium ions in HMPA¹⁶ (-741 to 814 kJ/mol). The large proton hydration enthalpy, as compared to sodium solvation enthalpies in THF and HMPA, could account for this difference (see text below).

Since the absolute heat of hydration of H⁺ has been previously estimated as -1090.8 ± 10.5 kJ/mol²⁶ by the method of Halliwell and Nyburg,²⁷ the single-ion heats of hydration for BQ^{•-} and NQ^{•-} can also be estimated by subtracting the heat of proton hydration to the heats of hydration of the semiquinone, H⁺ pairs. Thus, the single-ion enthalpies of hydration of BQ^{•-} and NQ^{•-} are estimated as -360 and -377 kJ/mol, respectively. The hydration of these semiquinones are as exothermic as those corresponding to Cl⁻ ($\Delta H^\circ_{\text{hydr}} = -376$ kJ/mol) or NO₂⁻ ($\Delta H^\circ_{\text{hydr}} = -366$ kJ/mol) although less exothermic than that corresponding to acetate ($\Delta H^\circ_{\text{hydr}} = -423$ kJ/mol).²⁸ These single-ion heats of hydration can be compared to the single-ion heats of solvation of BQ^{•-} and NQ^{•-} in HMPA. The heats of solvation of BQ^{•-}, Na⁺ and NQ^{•-}, Na⁺ in HMPA, where ion association does not exist, were previously determined to be -755 ± 10 and -757 ± 22 kJ/mol, respectively.¹⁶ If the single-ion enthalpy of solvation of the sodium cation in HMPA, -452 kJ/mol,²⁹ is subtracted from the heats of solvation of the semiquinone, Na⁺ pairs indicated above, single-ion enthalpies of solvation in HMPA of -303 and -305 kJ/mol for BQ^{•-} and NQ^{•-}, respectively, are obtained. Thus, stronger interactions between the semiquinones and water than with HMPA is occurring probably due to sterical inhibition of the methyl groups in the HMPA molecule, which prevent a close approach of the semiquinones to the electropositive phosphorus.³⁰ This type of inhibition does not exist in water. However, other considerations like polarity of the solvent, hydrogen bonding in water, and differences in solvation structure need to be considered to explain these differences in single-ion heats of solvation upon going from water to HMPA.

The estimated single-ion heats of solvation of anthracene³¹ and naphthalene¹² radical ions in HMPA, -301 and -293 kJ/mol, respectively, are within the range of those corresponding to semiquinones in HMPA¹⁶ (289-362 kJ/mol) although also less negative than the single-ion heats of hydration of BQ^{•-} and NQ^{•-} determined here.

The enthalpies of disproportionation of both BQ^{•-} and NQ^{•-} in the gas phase were also obtained through the thermochemical cycle depicted on Table III. The heat of sublimation of NQH₂

(26) Marcus, Y. *Ion Solvation*; Wiley: New York, 1985; p 110.

(27) Halliwell, D. F.; Nyburg, S. C. *Trans. Faraday Soc.* **1963**, *59*, 1126.

(28) NBS Tables of Chemical Thermodynamic Properties. *J. Phys. Chem. Ref. Data, Suppl.* **2** **1982**, *11*.

(29) Stevenson, G. R.; Valentin, J.; Williams, E.; Caldwell, G.; Alegria, A. E. *J. Am. Chem. Soc.* **1979**, *101*, 515.

(30) Normant, H. *Angew. Chem., Int. Ed. Engl.* **1967**, *1046*.

(31) Stevenson, G. R.; Williams, E., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 5910.

TABLE III: Thermochemical Cycle Used in the Determination of the Heat of Disproportionation of BQ^{•-} and NQ^{•-} in the Gas Phase

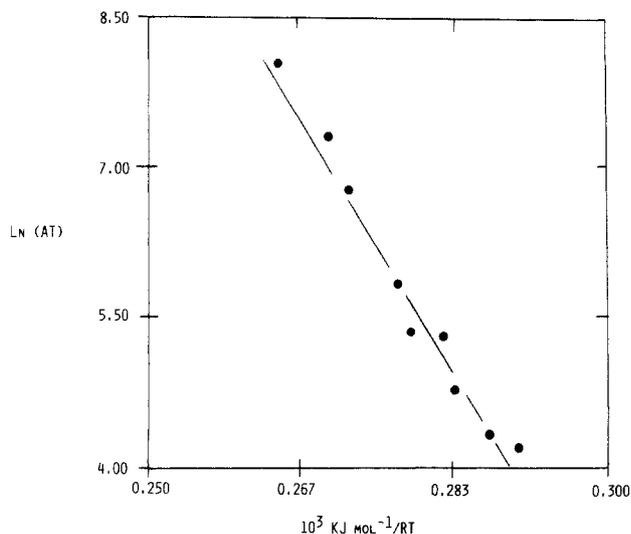
reaction	$\Delta H^\circ / (\text{kJ mol}^{-1})$	
	BQ	NQ
$2\text{Q}^{\bullet-}(\text{g}) + 2\text{H}^+(\text{g}) \rightarrow 2\text{Q}^{\bullet-}(\text{aq}) + 2\text{H}^+(\text{aq})$	-2901 ± 15	-2935 ± 23
$2\text{Q}^{\bullet-}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow \text{QH}_2(\text{aq}) + \text{Q}(\text{aq})$	-72.2 ± 0.3	-58 ± 2
$\text{QH}_2(\text{aq}) \rightarrow \text{QH}_2(\text{s})$	-18.4 ± 0.6	-22 ± 1
$\text{Q}(\text{aq}) \rightarrow \text{Q}(\text{s})$	-17 ± 3	-4 ± 2
$\text{QH}_2(\text{s}) \rightarrow \text{QH}_2(\text{g})$	$+99 \pm 2^a$	$+150 \pm 8^b$
$\text{Q}(\text{s}) \rightarrow \text{Q}(\text{g})$	$+63 \pm 3$	$+73 \pm 4$
$2\text{Q}^{\bullet-}(\text{g}) + 2\text{H}^+(\text{g}) \rightarrow \text{QH}_2(\text{g}) + \text{Q}(\text{g})$	-2847 ± 10^c	-2796 ± 22^c

^aFrom ref 21. ^bFrom this work. ^cThese errors are the result of subtracting the errors from the second, third, and fifth reaction enthalpies to that corresponding to the first reaction and adding the error corresponding to the fourth reaction enthalpy, since the subtracted errors are already considered in the uncertainty of the first reaction.

TABLE IV: Thermochemical Cycle Used in the Determination of the Heat of Hydration of the Negative Charge Plus H⁺ in 12.5 mM Cacodylic-Cacodylate Buffer, pH = 7.1

reaction	$\Delta H^\circ / (\text{kJ mol}^{-1})$	
	BQ	NQ
$\text{H}^+(\text{g}) + \text{Q}^{\bullet-}(\text{g}) \rightarrow \text{Q}^{\bullet-}(\text{aq}) + \text{H}^+(\text{aq})$	-1451 ± 8	-468 ± 12
$\text{Q}(\text{aq}) \rightarrow \text{Q}(\text{s})$	-17 ± 3	-4 ± 2
$\text{Q}(\text{s}) \rightarrow \text{Q}(\text{g})$	$+63 \pm 3$	$+73 \pm 4$
$\text{H}^+(\text{g}) + \text{Q}^{\bullet-}(\text{g}) + \text{Q}(\text{aq}) \rightarrow \text{Q}^{\bullet-}(\text{aq}) + \text{Q}(\text{g}) + \text{H}^+(\text{aq})$	1405 ± 2	1399 ± 6

^aThe errors from the second and third reactions are subtracted from that corresponding to the first one since the former reactions are included in the thermochemical cycle used in obtaining the heat of the first reaction.

**Figure 4.** Graph used in the determination of the enthalpy of sublimation of NQH₂.

needed for this cycle was determined as described in the Experimental Section. A plot of the logarithm of the product of the absorbance times the absolute temperature against $10^3/RT$ yielded a straight line from which the enthalpy of sublimation of NQH₂, 150 ± 8 kJ/mol, was obtained, Figure 4.

The enthalpies of disproportionation of BQ^{•-} and NQ^{•-} in the gas phase are both more negative (by a factor of approximately 40) than the corresponding ones in the aqueous phase. This is expected, since the strong water-ion interactions do not exist in the gas-phase reaction. While the enthalpies of disproportionation are much more negative for both semiquinones in the gas phase as compared to the aqueous solution, a similar trend in the relative magnitudes of the enthalpies of disproportionation is observed in

both the aqueous and the gas phase, i.e., BQ^{•-} follows a more exothermic disproportionation than NQ^{•-} in both phases. However, the difference between the enthalpies of disproportionation corresponding to BQ^{•-} and NQ^{•-} is more accentuated in the gaseous ($-2796 + 2847 = 51$ kJ/mol) than in the aqueous ($-58 + 72.2 = 14.2$ kJ/mol) phase. Thus, hydration makes disproportionation approximately 2700 kJ/mol less exothermic in each case while the difference in the heats of disproportionation corresponding to BQ^{•-} and NQ^{•-} is lowered by $51 - 14.2 \approx 37$ kJ/mol. This clearly contrasts with other types of equilibria in which the spontaneity direction is reversed by solvation.^{8,9}

In order to detect if there is any difference in the actual charge hydration between BQ^{•-} and NQ^{•-}, the enthalpy of solvation of the corresponding neutral quinone is subtracted from the heat of hydration of the semiquinone and the proton, Table IV. Essentially, no difference is observed between the resulting enthalpies corresponding to BQ and NQ. A similar observation was made previously regarding the solvation of the semiquinone net negative charge in HMPA.¹⁶ Therefore, as explained in that work, the difference in the strength of hydration between BQ^{•-} and NQ^{•-} can be attributed to differences in the hydration of the molecular framework of Q^{•-} and not to differences in the solvation of the net negative charge.

In summary, this work represents the first utilization of heats of disproportionation as a means to obtain the heats of hydration of two π radical anions, i.e., 1,4-benzo- and 1,4-naphthosemiquinones at physiological pH. BQ^{•-} undergoes a more exergonic and exothermic disproportionation than NQ^{•-} in both aqueous and gas phases. Hydration makes the disproportionation of BQ^{•-} and NQ^{•-} approximately 2700 kJ/mol less exothermic while the difference in the corresponding heats of disproportionation is lowered by 14 kJ/mol.

Acknowledgment. We express appreciation to the NIH-MBRS program for support of this work with Grant RR08216.

Registry No. BQ^{•-}, 3225-29-4; NQ^{•-}, 20261-01-2; NQH₂, 571-60-8.