

# Redox and Acidity Properties of 4-Substituted Aniline Radical Cations in Water

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Received August 31, 1993\*

**Abstract:** By means of pulse radiolysis the one-electron reduction potentials of twelve 4-substituted aniline radical cations and the  $pK_a$  values of eight 4-substituted aniline radical cations have been determined. Both the potentials and the  $pK_a$  values were shown to be linearly dependent on the Brown  $\sigma_p^+$  values for the 4-substituents. The one-electron reduction potentials were also compared to previously reported electrochemically determined  $E_{1/2}$  values resulting in good agreement between the two sets of data. By combining the one-electron reduction potentials and the  $pK_a$  values the N–H bond dissociation energies of some 4-substituted anilines were calculated, also showing a linear substituent dependence. The absolute N–H bond dissociation energy of aniline found was close to a previously reported value.

## Introduction

The discussion of substituent effects on radical reactivity is of long standing.<sup>1</sup> The main issue considered was whether the observed effect is mainly due to thermochemical changes or whether it is the polarity of the transition state which is influenced. Starting with the pioneering work of Zavitsas and Pinto<sup>2</sup> and Mahoney and DaRooge,<sup>3</sup> the overriding importance of bond strength changes with the substituent has been substantiated by the direct calorimetric work of Mulder et al.<sup>4</sup> on phenols. Their work was subsequently corroborated and extended by Lind et al.<sup>5</sup> and Bordwell and Cheng.<sup>6</sup>

Since the general settling of this issue is contingent on a good knowledge of bond strengths, it is vital to determine the latter with sufficient accuracy. The combination of reduction potential and acidity in a thermochemical cycle, described in several publications,<sup>7–9</sup> is a facile and accurate method of determining these quantities.

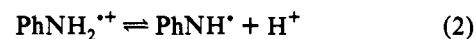
In principle, the most accurate method should be the one providing thermodynamic reduction potentials, such as pulse radiolysis. Clearly, nonthermodynamic electrochemical methods are often satisfactory, but without "calibration" against a thermodynamic method some lingering doubt as to the reliability of the former always remains. To date, only a few bond types have been investigated with respect to remote, e.g. para, substituents. These comprise phenolic O–H,<sup>4–6</sup> benzylic C–H,<sup>10,11</sup> benzylic C–Br,<sup>12</sup> and anisolic C–O<sup>13</sup> bonds, as well as the S–C<sup>14</sup>

bond in phenyl thioether radicals. In the present work we intend to add the 4-substituted anilines to this list.<sup>50a</sup> Obviously, the latter are of both basic chemical and biological importance.

One-electron oxidation of anilines initially results in the formation of aniline radical cations. This (reaction 1) can easily



be accomplished by using radiation chemical methods, e.g. pulse radiolysis. A radiolytically formed oxidant is exemplified by  $\text{N}_3^*$  in reaction 1. The cations thus formed can undergo deprotonation (reaction 2) to yield the corresponding anilino radical. These two



equilibria are characterized by the one-electron reduction potential and the  $pK_a$  value, respectively. The unsubstituted aniline radical cation and the anilino radical have been thoroughly characterized previously, using several different spectroscopical methods.<sup>15–18</sup>

The one-electron reduction potentials for 4-substituted phenoxyl radicals,<sup>5</sup> multisubstituted phenoxyl radicals,<sup>19</sup> and 1,4-disubstituted benzene radical cations<sup>20</sup> have been shown to follow linear free energy relationships. Since 4-substituted aniline radical cations belong to the family of 1,4-disubstituted benzene radical cations, one would expect them to follow the general relationship derived<sup>20</sup> for this family of compounds (eq 3) where  $\sigma_{p1}^+$  and  $\sigma_{p4}^+$

$$E^\circ = 2.2 + 0.8(\sigma_{p1}^+ + \sigma_{p4}^+) + 0.4\sigma_{p1}^+ \sigma_{p4}^+ \quad (\text{V vs NHE}) \quad (3)$$

are the Brown constants of the substituents in position 1 and 4. From the symmetry of eq 3 it can be seen that the 1- and 4-positions can be chosen arbitrarily.

With the exception of the values for some substituted phenoxyl radical cations,<sup>21</sup> unsubstituted aniline radical cation,<sup>18</sup> and the 4-sulfanilic acid radical cation,<sup>22</sup> no other  $pK_a$  values for aromatic

\* Abstract published in *Advance ACS Abstracts*, February 1, 1994.

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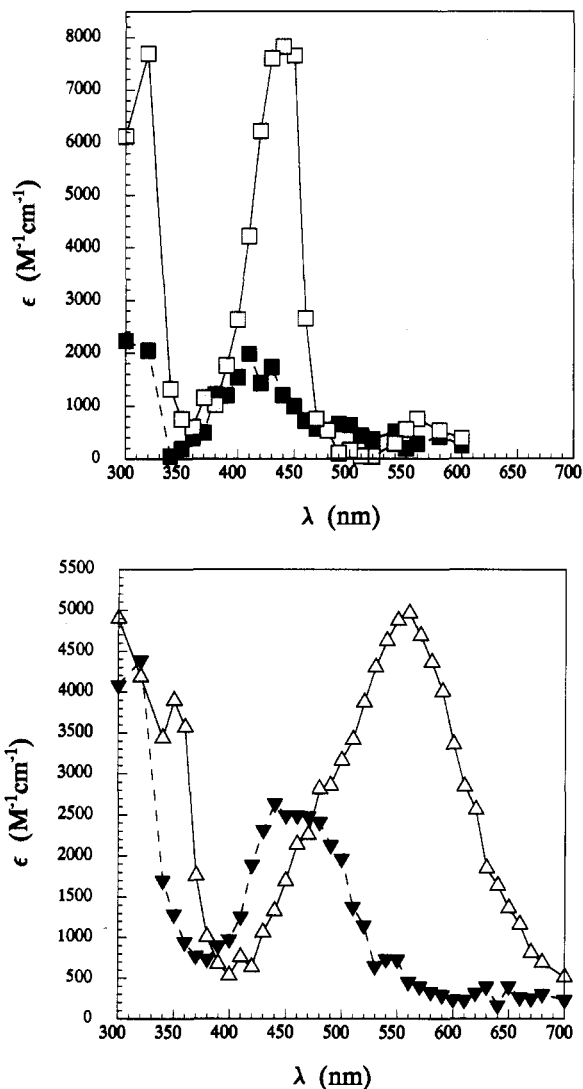
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**Figure 1.** (a, Top) Optical spectra of the 4-methylaniline radical cation ( $\square$ ) and the 4-methylanilino radical ( $\blacksquare$ ). (b, Bottom) Optical spectra of the 4-iodoaniline radical cation ( $\triangle$ ) and the 4-iodoanilino radical ( $\blacktriangledown$ ).

radical cations in water appear to have been reported. As was mentioned, the relative X-H bond dissociation energy for a given compound can be calculated by using the one-electron reduction potential vs NHE ( $E^\circ$ ) and the  $pK_a$  value. These quantities are related through eq 4, where  $C$  is somewhat solvent dependent<sup>23,24</sup>

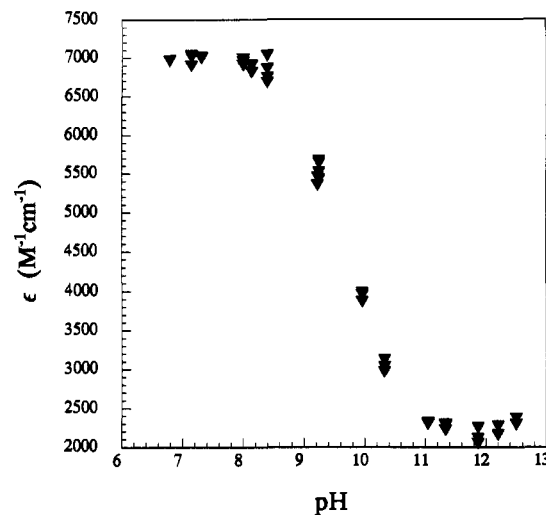
$$D(X-H) = 96.48E^\circ + 5.70pK_a + C \quad (\text{kJ/mol}) \quad (4)$$

but is assumed to be unaffected by the substituent. This indirect method of determining bond dissociation energies has been successfully used for substituted phenols in water<sup>5</sup> as well as in organic solvents.<sup>6</sup> Also, a linear substituent-dependent relationship was found for phenolic O-H bond dissociation energies.<sup>4-6</sup>

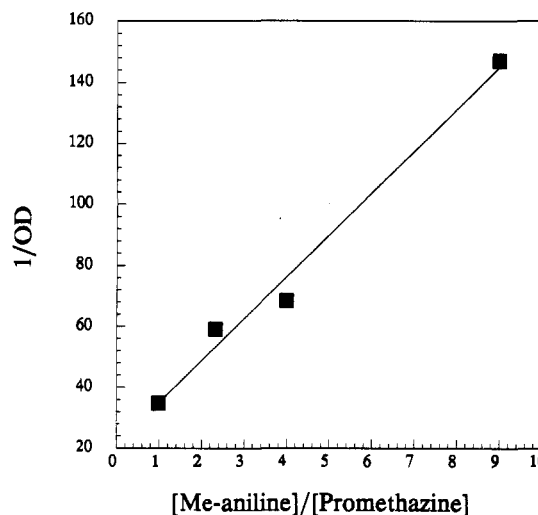
In this work we have determined the one-electron reduction potentials and the  $pK_a$  values of a number of 4-substituted aniline radical cations by means of pulse radiolysis.

### Experimental Section

All chemicals of the purest grade available (Aldrich and Merck) were used as supplied with the exception of aniline which was distilled prior to use. Millipore Milli-Q filtered water was used throughout. Radiolysis of water results in the formation of  $\text{OH}^\bullet$ ,  $e_{\text{aq}}^-$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2$ , and  $\text{H}_3\text{O}^+$ , with  $\text{OH}^\bullet$  and  $e_{\text{aq}}^-$  being the major radical species with primary radiation chemical yields of  $0.28 \mu\text{mol/J}$  each<sup>25</sup> above pH 3.  $\text{N}_2\text{O}$ -saturated



**Figure 2.** pH titration curve for the 4-methoxyaniline radical cation (440 nm).

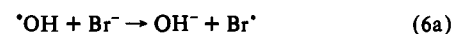


**Figure 3.** The inverse of the measured optical density at equilibrium as a function of the ratio between 4-methylaniline and promethazine (525 nm).

solutions were used throughout in order to convert the reducing solvated electron into the oxidizing hydroxyl radical<sup>25</sup> ( $G_{\text{OH}} = 5.6 \times 10^{-7} \text{ mol/J}$ ).

The pulse radiolysis equipment consists of a linear accelerator delivering 3-MeV electrons and a computerized optical detection system.<sup>26</sup> The pulses were of 5–10-ns duration giving doses of 3–6 Gy. For dosimetry a  $\text{N}_2\text{O}$ -saturated  $10^{-2} \text{ M}$  KSCN solution was used.<sup>27</sup> The  $G_{\epsilon}$  value of  $(\text{SCN})_2^{\bullet-}$  was taken to be  $4.78 \times 10^{-4} \text{ mol}^2/\text{J}$  at 500 nm.

Primary oxidation of the 4-substituted anilines was carried out by  $\text{N}_3^\bullet$  when working at pH values above the  $pK_a$  of  $\text{HN}_3$  ( $pK_a = 4.7$ ). When working at pH values near or below 4.7  $\text{Br}_2^{\bullet-}$  was used for the primary oxidation of the 4-substituted anilines. These two primary oxidants were produced in the following way upon irradiation.



The above reactions had the following rate constants:  $k_5 = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>28</sup>  $k_{6a} = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>28</sup> and  $k_{6b} = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>29</sup> respectively. The concentrations of  $\text{N}_3^-$  and  $\text{Br}^-$  were  $10^{-2}$  and  $0.1 \text{ M}$ ,

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Table 1. Experimental Conditions and Reduction Potential Measurements

4-substituted aniline (concn, M)	primary oxidant	pH	ref substance (concn, M)	$\lambda$ (nm)
PhNH <sub>2</sub> (10 <sup>-3</sup> )	N <sub>3</sub> <sup>•</sup>	5.7	promethazine	525
4-NH <sub>2</sub> -PhNH <sub>2</sub> (5 × 10 <sup>-6</sup> -10 <sup>-3</sup> )	N <sub>3</sub> <sup>•</sup>	11	4-CH <sub>3</sub> -PhO <sup>-</sup> (5 × 10 <sup>-4</sup> -10 <sup>-3</sup> )	480
4-HO-PhNH <sub>2</sub> (5 × 10 <sup>-6</sup> -10 <sup>-3</sup> )	N <sub>3</sub> <sup>•</sup>	5.6	promethazine (10 <sup>-3</sup> )	525
4-CH <sub>3</sub> -PhNH <sub>2</sub> (5 × 10 <sup>-4</sup> -10 <sup>-3</sup> )	N <sub>3</sub> <sup>•</sup>	5.7	promethazine	525
4-(CH <sub>3</sub> ) <sub>3</sub> C-PhNH <sub>2</sub> (5 × 10 <sup>-4</sup> -10 <sup>-3</sup> )	N <sub>3</sub> <sup>•</sup>	5.7	promethazine	525
4-CH <sub>3</sub> O-PhNH <sub>2</sub> (5 × 10 <sup>-5</sup> -10 <sup>-3</sup> )	N <sub>3</sub> <sup>•</sup>	5.7	promethazine	525
4-I-PhNH <sub>2</sub> (2 × 10 <sup>-4</sup> -10 <sup>-3</sup> )	N <sub>3</sub> <sup>•</sup>	5.8	PhNH <sub>2</sub> (2 × 10 <sup>-4</sup> -10 <sup>-3</sup> )	560
4-CH <sub>3</sub> CO-PhNH <sub>2</sub>	N <sub>3</sub> <sup>•</sup>	5.5	4-I-PhNH <sub>2</sub> (5 × 10 <sup>-6</sup> -10 <sup>-3</sup> )	560
4-Cl-PhNH <sub>2</sub> (2 × 10 <sup>-4</sup> -10 <sup>-3</sup> )	N <sub>3</sub> <sup>•</sup>	5.8	4-I-PhNH <sub>2</sub> (2 × 10 <sup>-4</sup> -10 <sup>-3</sup> )	560
4-Br-PhNH <sub>2</sub> (2 × 10 <sup>-4</sup> -10 <sup>-3</sup> )	N <sub>3</sub> <sup>•</sup>	5.8	4-I-PhNH <sub>2</sub> (2 × 10 <sup>-4</sup> -10 <sup>-3</sup> )	560
4-CF <sub>3</sub> -PhNH <sub>2</sub>	Br <sub>2</sub> <sup>-</sup>	3	1,4-dimethoxybenzene (5 × 10 <sup>-4</sup> -10 <sup>-3</sup> )	460
4-CN-PhNH <sub>2</sub> (5 × 10 <sup>-4</sup> -10 <sup>-3</sup> )	Br <sub>2</sub> <sup>-</sup>	3	1,4-dimethoxybenzene (5 × 10 <sup>-4</sup> -10 <sup>-3</sup> )	460

respectively. The use of OH<sup>•</sup> for oxidation of the anilines was avoided, it being known to participate in reactions other than one-electron oxidation. The reduction potential measurements were performed at pH values lying between the pK<sub>a</sub> of the 4-substituted anilinium cation and that of its corresponding radical cation. Phosphate buffers, borate buffer, sulfuric acid, and NaOH were used to adjust the pH.

**Methods.** The optical spectra of the 4-substituted aniline radical cations and the corresponding 4-substituted anilino radicals differ markedly (see Figure 1, a and b), making determination of radical cation pK<sub>a</sub> values possible. The pK<sub>a</sub> curve is obtained by simply measuring the absorbance at a suitable wavelength for a number of different pH values (see Figure 2) and allowing for differences in the dose.

The one-electron reduction potentials of the 4-substituted aniline radical cations were determined by measuring the equilibrium concentrations of radical cations or the radicals formed upon oxidation of the reference substance, with varying concentrations of 4-substituted aniline and reference substance (reaction 7).<sup>30</sup> The resulting equilibrium concen-



trations yield the equilibrium constant which can be inserted into the Nernst equation to calculate the one-electron reduction potential. The overwhelming majority of the redox partners employed, including promethazine<sup>33</sup> [10-(2-(dimethylamino)propyl)phenothiazine], undergo the same charge change as the PhNH<sub>2</sub><sup>•+</sup>/PhNH<sub>2</sub> couples, i.e., the charge changes from 0 to +1 during oxidation. Consequently the equilibrium constant  $K_7$  can, to a good approximation, be regarded as independent of the ionic strength. Thus, failure to extrapolate to zero ionic strength should not introduce any appreciable error. The rates of equilibration can also be measured and used to obtain a kinetically determined equilibrium constant.

Equilibrium constants are preferably determined by plotting 1/OD (OD = optical density at equilibrium) or  $k_{\text{obs}}$  against the ratio between the concentrations of 4-substituted aniline and reference substance (see Figure 3). The equilibrium constant is obtained from the following equation

$$1/\text{OD} = \{1 + [\text{reference substance}] / (K[\text{4-substituted aniline}])\} / \text{OD}^\circ \quad (8)$$

which can be shown to hold for the equilibrium (reaction 7). OD<sup>°</sup> is the maximum signal obtainable. The forward and reverse rate constants used to calculate the "kinetic" equilibrium constant were determined by using the following relationship:

$$k_{\text{obs}} = k_f[\text{4-substituted aniline}] + k_r[\text{reference substance}] \quad (9)$$

In Tables 1 and 2 the experimental conditions for the reduction potential and the pK<sub>a</sub> measurements are given. The reference substances (reduced form given) employed were 4-CH<sub>3</sub>-PhO<sup>-</sup>, promethazine, and 1,4-dimethoxybenzene, their one-electron reduction potentials versus NHE being 0.68,<sup>5</sup> 0.91 (see next section) and 1.30 V,<sup>20</sup> respectively. Promethazine was used as the reference substance in a rather broad potential interval due to the lack of other suitable reference couples. Nevertheless,

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(30) The pioneering work in this field was performed by Arai and Dorfman.<sup>31</sup> An excellent review is given in ref 32.

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(33) Even though promethazine formerly undergoes a charge change from +1 to +2 (due to a charged side chain), the reactive center changes its charge from 0 to +1 during oxidation.

Table 2. Measuring Wavelengths for pK<sub>a</sub> Measurements

4-substituted aniline	$\lambda$ (nm)
4-CH <sub>3</sub> CO-PhNH <sub>2</sub>	470
4-NH <sub>2</sub> -PhNH <sub>2</sub>	480
4-CH <sub>3</sub> -PhNH <sub>2</sub>	440
4-(CH <sub>3</sub> ) <sub>3</sub> C-PhNH <sub>2</sub>	450
4-CH <sub>3</sub> O-PhNH <sub>2</sub>	440
4-I-PhNH <sub>2</sub>	560
4-CF <sub>3</sub> -PhNH <sub>2</sub>	440
4-CN-PhNH <sub>2</sub>	440

we believe these measurements to be rather accurate, due to the high stability of the radical formed upon one-electron oxidation of promethazine.

## Results and Discussion

Table 3 compiles the redox equilibrium constants,  $K_{\text{OD}}$  and  $K_{\text{kin}}$  (derived using the two methods previously described), the one-electron reduction potentials,  $E^\circ$  (4-Z-PhNH<sub>2</sub><sup>•+</sup>/4-Z-PhNH<sub>2</sub>), and pK<sub>a</sub> values determined in this work along with previously reported data.

**One-Electron Reduction Potentials.** The one-electron reduction potential of the aniline radical cation determined in this work is lower by 20 mV than a previously reported value,<sup>34</sup> this difference, however, being within experimental error. Since all reduction potentials, with the exception of those for 4-CF<sub>3</sub>, 4-NH<sub>2</sub>, and 4-CN-substituted aniline, are internally related by the choice of reference substance we feel quite confident that the relative effect of 4-substitution on the reduction potentials is reliably reproduced.

Due to the great variation in reported values<sup>32,35</sup> of the potential of promethazine we thoroughly remeasured it using 2,3-dimethylindole ( $E^\circ = 0.93$  V<sup>36</sup>) as reference. Previously  $E^\circ$  of 2,3-dimethylindole was determined against the ClO<sub>2</sub>/ClO<sub>2</sub><sup>-</sup> couple (0.936 V<sup>37</sup>) and was extrapolated to zero ionic strength. The potential was determined to be 0.91 V vs NHE which is close to a previously given value of 0.90 V.<sup>32</sup> However, it is higher than 0.865 V, the recommended value in ref 32. We note that in ref 35, where the redox equilibrium between promethazine and IrCl<sub>6</sub><sup>2-</sup>/IrCl<sub>6</sub><sup>3-</sup> (the latter having the well-known value of  $E^\circ = 0.867$  V<sup>38</sup>) was investigated, a much higher value, namely 0.98 V, was derived for  $E^\circ$  (promethazine). We could confirm this value within 20 mV in a similar system. Clearly, the apparent one-electron reduction potential of promethazine is strongly dependent on the charge of the redox partner and on the ionic strength of the solution, implying that promethazine should always be calibrated for the conditions used. As the oxidation of PhNH<sub>2</sub>, 2,3-dimethylindole, and promethazine involves a charge change from 0 to +1 we believe the utilized  $E^\circ$  (promethazine) to be proper in the present system. The latter value is already extrapolated to zero ionic strength. In Figure 4 we plot the

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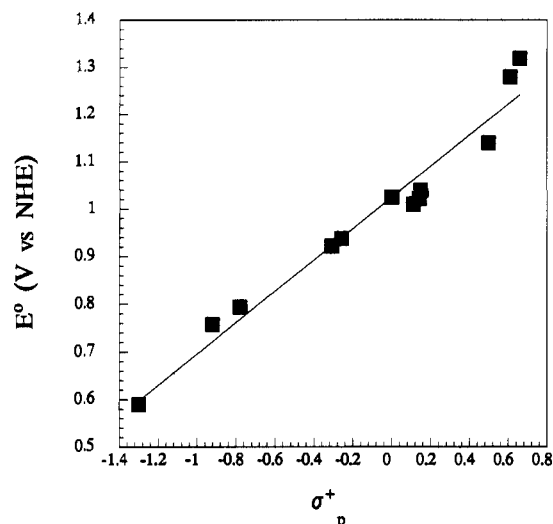
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**Table 3.** Equilibrium Constants, One-Electron Reduction Potentials, and  $pK_a$  Values

radical cation	$K_{OD}$	$K_{kin}$	$E^\circ(\text{PhNH}_2^{+\bullet}/\text{PhNH}_2)^a$ (V vs NHE)	$pK_a^b$
PhNH <sub>2</sub> <sup>•+</sup>	73.2	23	1.02	7.05 <sup>18</sup>
4-SO <sub>3</sub> <sup>-</sup> -PhNH <sub>2</sub> <sup>•+</sup>				5.8 <sup>22</sup>
4-HO-PhNH <sub>2</sub> <sup>•+</sup>	$2.9 \times 10^{-3}$	$2.7 \times 10^{-3}$	0.76	
4-NH <sub>2</sub> -PhNH <sub>2</sub> <sup>•+</sup>	$3.0 \times 10^{-2}$	$2.7 \times 10^{-2}$	0.59	$12 \pm 0.5$
4-CH <sub>3</sub> O-PhNH <sub>2</sub> <sup>•+</sup>	$9.3 \times 10^{-3}$	$6.7 \times 10^{-3}$	0.79	9.6
4-CH <sub>3</sub> -PhNH <sub>2</sub> <sup>•+</sup>	1.5	2.2	0.92	8.5
4-CH <sub>3</sub> -PhNH <sub>2</sub> <sup>•+</sup>	1.5	2.2	0.92	8.5
4-(CH <sub>3</sub> ) <sub>3</sub> C-PhNH <sub>2</sub> <sup>•+</sup>	3.2	2.5	0.94	8.2
4-CH <sub>3</sub> CO-PhNH <sub>2</sub> <sup>•+</sup>	108	20	$1.14 \pm 0.04$	6.1
4-I-PhNH <sub>2</sub> <sup>•+</sup>	1.0	1.2	1.02	7.1
4-Cl-PhNH <sub>2</sub> <sup>•+</sup>	0.68	0.3	1.01	
4-Br-PhNH <sub>2</sub> <sup>•+</sup>	2.2	4.2	1.04	
4-CF <sub>3</sub> -PhNH <sub>2</sub> <sup>•+</sup>	0.46	0.80	1.28	4.8
4-CN-PhNH <sub>2</sub> <sup>•+</sup>	2.2		1.32	$4 \pm 0.5$

<sup>a</sup> The reduction potentials are based exclusively on the  $K_{OD}$  values since these were technically easier to obtain under reproducible conditions. The uncertainties are estimated to be  $\pm 0.02$  V at most, unless otherwise stated. <sup>b</sup> Without going into detail we estimate the uncertainties due to failure to correct for ionic strength to be  $\pm 0.2$  pH units unless otherwise stated.



**Figure 4.** One-electron reduction potentials of the 4-substituted aniline radical cations studied in this work as a function of the Brown  $\sigma_p^+$  substituent constants.

measured reduction potentials against the Brown  $\sigma_p^+$  values of the 4-substituents. As can be seen the relationship between  $E^\circ$  and  $\sigma_p^+$  is linear and results in the following equation.

$$E^\circ = 1.02 + 0.33\sigma_p^+ \quad (\text{V vs NHE}) \quad R^2 = 0.98 \quad (10)$$

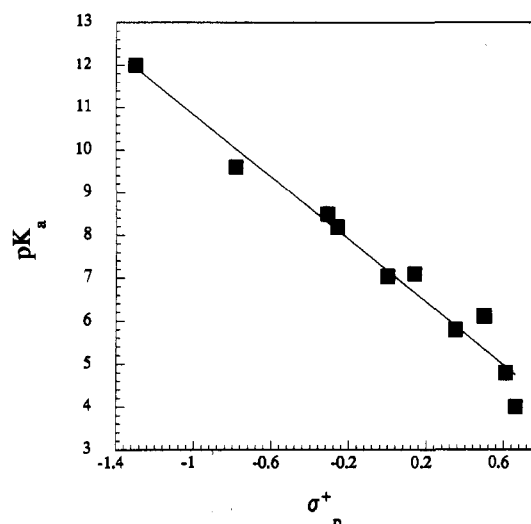
The slope is close to 0.28, the value predicted from the general equation for one-electron reduction potentials of 1,4-disubstituted benzene radical cations<sup>20</sup> (eq 11).

$$dE^\circ/d\sigma_{p4}^+ = 0.8 + 0.4\sigma_{p1}^+ \quad (11)$$

$\sigma_{p1}^+$  refers to the substituent at position 1, i.e. OH for phenols and NH<sub>2</sub> for anilines. Equation 11 is the derivative of eq 3.

Note also that the reduction potentials of the 4-(trifluoromethyl)4-CF<sub>3</sub>- and the 4-CN-substituted aniline radical cations are higher than predicted by eq 10. The good fit of the point for 4-OH-substituted aniline is remarkable, given the fact that this value was measured at pH 5.6. As the  $pK_a$  of the hydroquinone radical cation is ca.  $-1$ ,<sup>21</sup> we would expect the corresponding 4-aminophenoxy radical cation to deprotonate around pH 0. Thus, at pH 5.6 we most probably have the neutral 4-aminophenoxy radical, whence the good fit would appear to be fortuitous.<sup>50b</sup>

A comparison of the reduction potentials determined in this work with the "half-wave" potentials determined electrochemically in water by Bacon and Adams<sup>39</sup> shows that the results obtained by pulse radiolysis or polarography agree within ca. 100 mV (0.67, 0.97, 0.98, and 1.28 V (ref 39) compared to 0.79, 1.02,



**Figure 5.**  $pK_a$  values of 4-substituted aniline radical cations determined in this work as a function of the Brown  $\sigma_p^+$  substituent constants.

1.01, and 1.32 V (this work) for 4-CH<sub>3</sub>O-PhNH<sub>2</sub>, PhNH<sub>2</sub>, 4-Cl-PhNH<sub>2</sub> and 4-CN-PhNH<sub>2</sub>, respectively). This is noteworthy, since the pulse radiolytic method is based on reversible redox reactions while its electrochemical counterpart involves irreversible oxidation. This close correspondence between the two independent potential determinations and a previously reported<sup>34</sup> pulse radiolytic determination of the one-electron reduction potential of the aniline radical cation implies that the value estimated by Pearson<sup>40</sup> (0.46 V vs NHE), based on thermodynamic calculations using gas-phase data and solvation energies, is almost certainly erroneous. This discrepancy probably derives from the use of inaccurate thermodynamical data in the gas phase.

**$pK_a$  Values.** In Figure 5 the  $pK_a$  values of the 4-substituted aniline radical cations determined in this work along with two previously reported  $pK_a$  values of 4-substituted aniline radical cations are plotted against the Brown  $\sigma_p^+$  values of the 4-substituents. As can be seen, the  $pK_a$  values are linearly dependent on the substituent constants. The following equation (eq 12) describes this linear dependence.

$$pK_a = 7.17 - 3.66\sigma_p^+ \quad R^2 = 0.98 \quad (12)$$

In water, the  $pK_a$  values of aniline radical cations are more sensitive toward the para substituent than those of the corresponding phenol<sup>21</sup> and 5-substituted indolyl<sup>41</sup> radical cations.

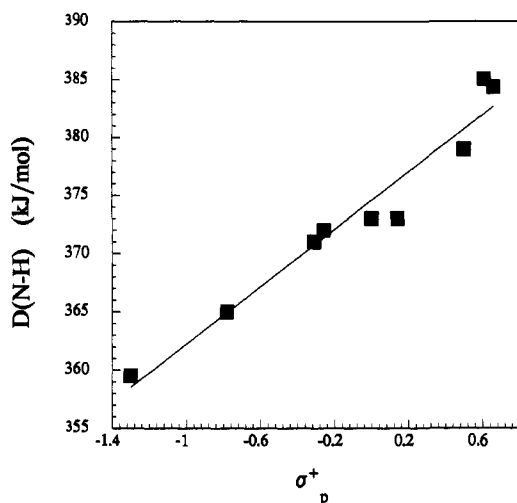
**N-H Bond Dissociation Energies.** The bond dissociation energies can be calculated using eq 4. In water  $C = \Delta G^\circ_r(\text{H}^\bullet)_g + TS^\circ(\text{H}^\bullet)_g + T(S^\circ(\text{N}^\bullet)_g - S^\circ(\text{NH})_g) - \Delta\Delta G^\circ_{g-aq}$ . Here, H<sup>•</sup>,

(40) Pearson, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 6109.

(41) Jovanovic, S. V.; Steenken, S. *J. Phys. Chem.* **1992**, *96*, 6674.

Table 4. Bond Dissociation Enthalpies

substance	$D(\text{N-H})$ (kJ/mol)
PhNH <sub>2</sub>	373
4-NH <sub>2</sub> -PhNH <sub>2</sub>	360
4-CH <sub>3</sub> O-PhNH <sub>2</sub>	365
4-CH <sub>3</sub> -PhNH <sub>2</sub>	371
4-(CH <sub>3</sub> ) <sub>3</sub> C-PhNH <sub>2</sub>	372
4-CH <sub>3</sub> CO-PhNH <sub>2</sub>	379
4-I-PhNH <sub>2</sub>	373
4-CF <sub>3</sub> -PhNH <sub>2</sub>	385
4-CN-PhNH <sub>2</sub>	384

Figure 6. N-H bond dissociation enthalpies for 4-substituted anilines plotted against the Brown  $\sigma_p^+$  substituent constants.

$\text{N}^*$ , and  $\text{NH}$  denote the hydrogen atom, the anilino radical, and the parent aniline, respectively.  $g$  and  $aq$  refer to gaseous (1 atm) and aqueous (1 M) standard states. Finally,  $\Delta\Delta G_{g-aq}^\circ = \Delta G_{g-aq}^\circ(\text{N}^*) - \Delta G_{g-aq}^\circ(\text{NH})$ , where  $\Delta G_{g-aq}^\circ$  denotes the free energy of hydration. Utilizing the entropy values in ref 42 and neglecting  $\Delta\Delta G_{g-aq}^\circ$  we calculate the constant  $C$  to be 236.2 kJ/mol (56.45 kcal/mol). With this value for  $C$  an upper limit to the N-H bond dissociation energy is obtained, as the parent (NH), is expected to be more strongly hydrated (i.e. its  $\Delta G_{g-aq}^\circ$  is more negative) than the radical ( $\text{N}^*$ ). In fact, the most reasonable value of  $\Delta\Delta G_{g-aq}^\circ$  appears to be  $2 \pm 1$  kJ/mol, by which amount  $C$  should be reduced. This is based on an analysis of a similar problem by Armstrong et al.,<sup>43</sup> where the aqueous solvation of a primary alkylamine is shown to be only slightly, at most by 2 kJ/mol, stronger than that of a secondary alkylamine. Table 4 compiles the calculated bond dissociation enthalpies based on data from this work and from ref 18. In Figure 6 these same values are plotted against the Brown  $\sigma_p^+$  values of the 4-substituents. The substituent dependence for the N-H bond dissociation enthalpies is best described by eq 13.

$$D(\text{N-H}) = 375 + 12.1\sigma_p^+ \quad (\text{kJ/mol}) \quad R^2 = 0.97 \quad (13)$$

The best N-H bond dissociation energy for aniline is  $373 \pm 4$  kJ/mol ( $89 \pm 1$  kcal/mol), taking into account the previously mentioned difference in hydration energy. Here, 4 kJ/mol incorporates all uncertainties, including those of the redox standards. This value is in good agreement with  $368 \pm 8$  kJ/mol ( $88.0 \pm 2$  kcal/mol), recommended as the best gas-phase value in ref 44. However, the value estimated by Bordwell et al.,<sup>45</sup> 385

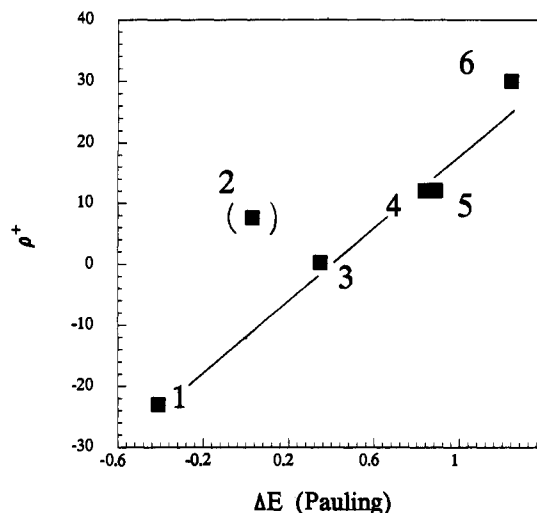
(42) Colussi, A. J.; Benson, S. W. *Int. J. Chem. Kinet.* **1978**, *10*, 1139.(43) Armstrong, D. A.; Rauk, A.; Yu, D. *J. Am. Chem. Soc.* **1993**, *115*, 666.(44) McMillen, D. F.; Golden, D. M. In *Annual Review of Physical Chemistry*; Rabinovitch, B. S.; Schurr, J. M.; Strauss, H. L., Eds.; Annual Reviews Inc.: Palo Alto, CA, 1982; Vol. 33.(45) Bordwell, F. G.; Cheng, J.-P.; Ji, G.-Z.; Satish, A. V.; Zhang, X.-M. *J. Am. Chem. Soc.* **1991**, *113*, 9790.

Figure 7. Bond dissociation energy remote substituent dependence as a function of electronegativity (Pauling) difference for (1) C-Br (benzyl bromides), (2) S-C (phenyl thioether radicals), (3) C-H (10-substituted 9-methylantracenes), (4) C-O (anisoles), (5) N-H (anilines), and (6) O-H (phenols).

$\pm 4$  kJ/mol ( $92 \pm 1$  kcal/mol), is somewhat higher than can be accounted for by the error margins.

The sensitivity of the R-X bond in 4-ZPhRX compounds toward the Z para substituents has been suggested<sup>12</sup> to increase with increasing difference between the electronegativities of R and X, forming the covalent bond. The rationale would be that the remote substituent mainly affects the energy of the parent and not that of the fragment radical containing R. We have plotted the substituent dependence,  $\rho^+$ , for the dissociation of O-H, C-H, S-C, C-Br, N-H, and C-O bonds for 4-substituted phenols,<sup>4-6</sup> phenyl thioether radicals,<sup>14,46</sup> benzyl bromides,<sup>12</sup> anilines, anisoles,<sup>13</sup> and 10-substituted 9-methylantracenes<sup>11</sup> against the electronegativity difference,  $\Delta E$ , according to both the Pauling and the Luo and Benson<sup>47</sup> electronegativity scales. The best linear fit was achieved using the Pauling scale<sup>48</sup> ( $R^2 = 0.82$  compared to  $R^2 = 0.79$ ). However,  $\rho^+$  for the S-C bond deviates from the general trend in both cases. Since the determinations of the S-C bond dissociation energies, being contingent on a number of assumptions, are fraught with some uncertainty<sup>49</sup> compared to those of the other R-X bond couples, we also make a comparison between substituent dependence and R-X electronegativity difference, excluding the S-C couple. The results show a much better linear correlation when using both the Pauling and the Luo and Benson electronegativity scales ( $R^2 = 0.97$  in both cases). In Figure 7 the resulting plot using the Pauling electronegativity scale and all the R-X couples is given. The resulting equation, excluding the S-C bond, is

$$\rho^+ = -11.3 + 30.3\Delta E \quad R^2 = 0.98 \quad (14)$$

where  $\rho^+$  is given in kilojoules. As can be seen, the N-H bond dissociation energy nicely conforms to the general trend.

**Acknowledgment.** We thank the Swedish Natural Science Research Council for financial support.

(46) Actually the addition product between methyl methacrylate and 4-substituted benzenethiyl radicals. Data were taken from ref 14.

(47) Luo, Y.-R.; Benson, S. W. *J. Phys. Chem.* **1988**, *92*, 5255.

(48) A referee rightly pointed out that a group electronegativity scale should be more appropriate than one based on free atoms. While we are preparing an analysis based on absolute electronegativities of bonded atoms, we cannot help noting that, despite its conceptual shortcomings, the scale of free atoms seems to work satisfactorily, i.e. the correlation using the electronegativities of bonded atoms is not markedly improved (submitted for publication).

(49) A provisional  $\rho^+$  value derived from the S-H dissociation energies of a limited number of 4-substituted thiophenols shows a better agreement with eq 14. Prof. D. A. Armstrong, University of Calgary, personal communications.(50) (a) This issue has also been addressed by Bordwell et al.: Bordwell, F. G.; Zhang, X.-M.; Cheng, J.-P. *J. Org. Chem.* **1993**, *58*, 6410. (b) A  $pK_a$  of 2.2 has been reported: Sun, Q.; Tripathi, G. N. R.; Schuler, R. H. *J. Phys. Chem.* **1990**, *94*, 6273.