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Homolytic Bond Cleavage Energies of the Acidic N-H Bonds in Dimethyl Sulfoxide Solution and Properties of the Corresponding Radicals and Radical Cations

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Abstract: *Homolytic bond dissociation energies (BDE) of various remotely-substituted and α-substituted aromatic amines in solution were estimated from a thermochemical cycle combining their equilibrium acidities (pK_{HA}) with the appropriate electrode potential data. The radical stabilization energies (RSE) derived from the relative BDE's indicated a general trend of radical destabilization by introducing an electron-withdrawing substituent onto either the remote or the alpha positions of the donor atom. This overall radical destabilization effect of an electron-withdrawing group is rationalized and discussed in terms of the element electronegativity and of the relative significance of the radical-stabilizing delocalization effect and the radical-destabilizing inductive effect. The acidities of the corresponding radical cations were also derived and their substituent effects are discussed as well.*

INTRODUCTION

Substituent effects on the stabilities of free radicals have long been an important issue in modern radical chemistry.[1] Data of this kind have been accumulated primarily from kinetic measurements of radical reactions involving mostly the benzylic carbon radicals through dual-parameter Hammett analysis ($\sigma^{\bullet}$'s).[1b] Although the $\sigma^{\bullet}$ scales obtained in the earlier years were not free from the difficulties in effectively separating the polar influence from the spin-delocalization effects and are consequently only fairly correlated to each other, the recent work by Jiang and co-workers[2] does provide reliable $\sigma^{\bullet}_{jj}$ data and the promising solution to the problems encountered in previous correlation studies. Despite the existing differences, a general trend was found which indicates a thermodynamic stabilization upon introducing either an electron-donating group (EDG) or an electron-withdrawing group (EWG) to the para-positions of the aromatic radicals investigated. Alternative means such as measurements of homolytic bond dissociation energies[3] or esr determinations of the changes in hyperfine coupling constants ($\sigma_\alpha^\bullet$)[1b] also provide the relevant information on radical stabilization energies. In fact most of the RSE data reported so far were derived from the relative bond strengths of their parent molecules and again the stabilizing abilities of EDG's and EWG's were observed in most cases. However, it is also noticed that this general phenomenon of substituent effects is not found without exceptions. An obvious example is that while the C-H bond in *Me*COCH$_2$-H is weaker than in *Me*CH$_2$-H (BDE 92 vs. 98 kcal/mol),[3] the O-H bond in *Me*COO-H is found *stronger* than that of its counterpart, *Me*O-H, by 7.8 kcal/mol (BDE 109.4 vs. 101.6),[4] indicating a radical *de*stabilizing effect of the acetyl group on the oxygen-centered radical. A comparison of the bond strengths of F$_3$C-H (106.7) with F$_2$CH-H (101)[3] casts further doubt on the generality of an EWG to stabilize even a carbon radical, even though the first and the second F atoms are indeed found stabilizing the methyl radical (BDE's of H$_3$C-H, FCH$_2$-H, and F$_2$CH-H are 105, 100, and 101, respectively).[3]

It is therefore of obvious significance to ask whether these exceptions were originated from the real nature of those radicals, and if so, what type of radicals may be expected to exhibit this kind of *opposite* effects of EDG and EWG on their thermodynamic stabilities. These questions, now still far from being answered, constitutes an important new aspect to the modern radical chemistry and certainly deserves more serious theoretical and experimental efforts. Since the majority of the studies on radical stabilities has so far focused only on the carbon-centered radicals and consequently left the behaviors of other radical families even less understood, our recent work reported in this paper on the nitrogen-centered radicals was designated to bring in a more inclusive spectrum of the substituent effects on the thermodynamic stabilities of radicals which covers a broader range of structural variations.

RESULTS AND DISCUSSION

A variety of α-substituted anilines with various substituent at the para-positions were investigated. Since nitrogen-centered radicals have not previously been thoroughly studied,[5] the selected group of nitrogen-containing compounds was expected to provide information on both the electronic effects of a remote substituent and the effect of the enhanced element electronegativity (by an α-EWG substitution) on the N-H BDE's as well as on the nitrogen radical cation acidities.

About the Methods. Solution homolytic bond dissociation energies were estimated for this family of substrates based on a thermochemical cycle (eqn. 1) using pK_A's in conjunction with the oxidation potentials of the

$$BDE = 2.303RTpK_{HA} + \mathcal{F}E_{ox}(A^-) + C \quad (1)$$

corresponding anions.[6] The constant C in eqn. (1) is 73.3 if the bond cleavage reaction is in dimethyl sulfoxide (DMSO) solution and the electrode potential is reported *vs*. the ferrocenium/ferrocene redox couple.[6b,10e] This general approach, *i.e.* using the electrode potential data to derive experimentally inaccessible information, has recently been applied to many chemically significant problems.[7-12] In this study, the radical stabilization energies (RSE) are accordingly discussed on the basis of the relative BDE's. This general method for deriving RSE's,[3] though has recently been questioned,[13] is found useful and reliable, at least as a first approximation, for estimating the RSE's for radicals derived from homolytic bond cleavage of many types of bonds (e.g. C-H, C-C, C-O bonds, etc.). A correlation of the C-H BDE's in the monosubstituted methanes, GCH_2-H, with the analogous C-C BDE's in GCH_2-CH_3 found in literature,[3] is fairly linear (r=0.954, slope =1.2), implying that the differences in ground-state energies are relatively unimportant in the majority of the cases previously reported. The difference in Hammett slopes between the correlations of the C-Br and C-H BDE's with σ^+, which was used as an argument in questioning the use of ΔBDE as a measure of the RSE,[13] is not observed in the comparisons of many C-C, C-S, and C-O bond strengths recently reported[12] with the C-H, S-H, and O-H bond energies. Eighteen families where the homolysis energies of both the X-C and X-H bonds (X=C, S, O) are available, were examined and the slopes of the BDE(X-C) vs. BDE(X-H) are generally found close to unity (1.03±0.2). The information gathered from most sources still seems to be in favor of using the ΔBDE as a guide to estimate the RSE in a relative sense for the majority of radicals. It should be noted, however, that the use of ΔBDE for deriving RSE's is not advised if substantial structural variations rather than the change of a remote substituent are involved in the comparison. In such cases, the negligence of the difference in ground state energies may cause significant error.

In order to apply eq 1, it was necessary to measure the pK_{HA}'s of the parent molecules and the oxidation potentials of the conjugate bases in solution. The former was accomplished using the "indicator overlapping" method[14] whereas the latter was obtained from cyclic voltammetric (CV) measurements (see Experimental Section). The pK_A values are believed to be accurate to ≤±0.1 pK unit (0.14 kcal/mol).[15] Although the experimental conditions, under which the CV of the nitranion was taken, did not provide reversible $E_{ox}(A^-)$'s, the potentials were reproducible to ≤±20 mV (0.6 kcal

Table 1. Homolytic N-H Bond Dissociation Energies of α-Substituted Anilines in methylsulfoxide Solution.

H-A	pK_{HA}[a]	$E_p^{ox}(A^-)/V$[b]	BDE[c]	ΔRSE[d]
$PhNH_2$	30.6	-0.992[e]	92.2[f]	(0)
$PhNHCOCH_3$	21.5	-0.159	98.9	-6.8
PhNHCOPh	18.8	-0.085	97.0	-4.9
$PhNHCOCF_3$	12.6	0.384	99.2	-7.1
$PhNHSO_2Ph$	11.9	0.136	92.6	-0.5
$PhNHCOCH_3$	21.5	-0.159	98.9	(0)
$4\text{-}OCH_3$	22.0	-0.348	95.3	3.6
$4\text{-}CH_3$	21.7_5	-0.254	97.1	1.8
4-Cl	20.3_5	-0.103	98.7	0.2
4-Br	20.3[g]	-0.082	99.1	-0.2
$4\text{-}COCH_3$	19.3[g]	0.019	100.0	-1.1
4-CN	18.6[g]	0.109	101.1	-2.3
$4\text{-}CF_3$	19.5[g]	0.078	101.6	-2.7
$4\text{-}NO_2$	17.6[g]	0.208	102.0	-3.2

[a] Equilibrium acidities in DMSO from ref. 15 unless otherwise noted. [b] Irreversible oxidation potentials measured by CV at a Pt electrode in 0.1M Bu_4NBF_4-DMSO *vs.* ferrocenium/ferrocene redox couple; substrate concentration: 1 mM, sweep rate: 100 mV/s. [c] Bond dissociation energies in kcal/mol derived using eqn. (1). [d] In kcal/mol (see text). [e] From ref. 5. [f] From ref. 9b. [g] Measured in this work.[18]

/mol). The BDE data thus derived, together with the quantities required in the evaluation, are presented in Table 1.

Homolysis of the N-H Bonds and the Relative Radical Stabilities. It is noteworthy, from the data in Table 1, that the N-H bond strength in aniline is increased by 0.5 to 7.1 kcal/mol upon substitution of an alpha electron-withdrawing group. While this bond-strengthening effect of the α-EWG is in striking contrast to the bond-weakening effect of the same α-EWG's on a C-H bond,[3] it is in line with the similar trend found in the MeO-H bond brought about by replacement of the methyl group with a MeCO group in the gas-phase.[4] This "abnormal behavior", which is against the commonly observed, may imply a fundamental difference in the substituent effects on the strengths of the BDE's or of the stabilities of the radicals resulted from homolysis. A further inspection of the table reveals that not only the N-H bond is strengthened by an α-EWG substitution, it is also strengthened if the EWG is introduced to the para-position of the aromatic ring. Based on the argument stated earlier, since the radical stabilization energies are most commonly represented by the relative BDE's,[3] it may be concluded that the anilino radical is stabilized by the EDG substitution but destabilized by the EWG substitution. The RSE data thus derived are listed in the last column of Table 1. This category of radicals, on which the effects of EDG and EWG operate in opposite directions, is classified by Walter as the "class *O*" radicals.[16] On the other hand, radicals where both the EDG and EWG show the similar stabilizing effects are called the "class *S*" radicals. This way of classifying radicals has not been verified previously due to the lack of relevant data. The results obtained in the present work appears to be an important experimental support for the class *S*/class *O* definition.

The substituent effects on the α-substituted nitrogen-centered radicals, based on the ΔBDE data, showed the same pattern as in the previously studied anilino radicals[5] and phenoxyl radicals.[91] The N-acetyl substitution in acetanilides generally causes a reinforcement of the stabilizing power of the *p*-EDG's as compared to that in the other two radical families but results in an attenuation of the destabilizing ability of the *p*-EWG's. The former is presumably caused by a greater electron-deficiency of the donor atom, whereas for the latter, due to a saturation effect. The comparison of

Table 2. Comparisons of Radical Stabilization Energies in DMSO Solution.[a]

Substituent	ΔRSE($ArNH_2$)[b]	ΔRSE(ArOH)[c]	RSE($ArNHCOCH_3$) (this work)
H	(0)	(0)	(0)
4-OCH_3	1.9	5.2	3.6
4-CH_3	0.3	1.2	1.8
4-Cl	-0.1	-0.4	0.2
4-$COCH_3$	-1.9	-2.9	-1.1
4-CN	-2.9	-4.4	-2.3
4-CF_3		-5.5	-2.7
4-NO_2	-4.4	-4.8	-3.2

[a] In kcal/mol. [b] Reference 5. [c] Reference 91.

the RSE's for aniline, phenol, and acetanilide families is given in Table 2.

The "dual substituent effect" suggested by Bordwell and co-workers,[9l,17] *i.e.* a substituent is expected to stabilize a radical through spin delocalization of the odd electron but to destabilize the radical in the meantime by virtue of its electron-withdrawing inductive effect on the electron-deficient donor atom, was used to rationalize the bond-strengthening effect by the electron-pulling group. While it certainly provides a deeper insight on the actual role of the substituents, this explanation is not sufficient as to foresee either the magnitude or the overall pattern (*i.e.* the class *S* or class *O* behavior) of the substituent effect. It is the authors' opinion that whether or not an EWG will destabilize a particular radical may depend upon the element electronegativity of the donor atom or the pair of electrons (could be *p* or π) residing in it or both. The common structural features observed with these families of radicals in Table 2, *i.e.* all having an electron lone pair on the donor atom that is more electronegative than carbon, are likely the candidates responsible for the apparent difference in the nature of the substituent effects on their BDE's. The possible role of the element electronegativity can be understood in terms of the enhanced electron-inductive destabilization by an EWG on a more electron-deficient center caused by its greater electronegativity of the donor atom which overrides the stabilizing effect obtained from the spin delocalization. On the other hand, it is also conceivable that the pair of electrons on the heteroatom radicals can be more effectively delocalized into the EWG than does the odd electron thus leaving the latter virtually more *localized*. If this is the case, the radical is expected to be less stable. The roles of the unshared pair of electrons and the element electronegativity in the pattern of radical substituent effect are still under current investigation.

Acidities of Radical Cations. The acidities of the corresponding cation radicals, which were derived using eq 2,[9a,c-e] are presented in Table 3. An

$$pK_{HA^{+\bullet}} = pK_{HA} + [E_{ox}(A^-) - E_{ox}(HA)] \times 23.06/1.37 \qquad (2)$$

examination of the table shows that these nitrogen radical cations are only moderately acidic, in sharp contrast to the super-acid acidities of the carbon-centered radical cations reported previously by Bordwell.[9a,c-e] The dramatic decrease in the acidities of the nitrogen radical cations as compared to those of the carbon radical cations is attributed to a much better accommodation of the positive charge by the nitrogen atom. The carbon radical cations, on the other hand, are not only incapable of providing this type of stabilization but are also being forced to lose the

Table 3. Acidities of α- and *para*-Substituted Aniline Radical Cations in DMSO Solution.

H-A	pK_{HA}[a]	$E_p^{ox}(A^-)/V$[b]	$E_p^{ox}(HA)/V$[b]	$pK_{HA}^{+\bullet}$[c]	$pK_{HA}^{+\bullet}(ArCH_2CN)$[d]
$ArNHCOCH_3$					$ArCH_2CN$
H	21.5	-.159	1.22	-1.8	-32
4-OCH_3	22.0	-.348	.91	0.8	-19
4-CH_3	21.7_5	-.254	1.13	-1.5	-28
4-Cl	20.3_5	-.103	1.36	-4.2	-31
4-Br	20.3	-.082	1.36	-3.9	
4-$COCH_3$	19.3	.019	1.42	-4.3	
4-CF_3	19.5	.078	1.56	-5.8	-38
4-CN	18.6	.109	1.65	-7.0	
4-NO_2	17.6	.208	1.66	-6.8	
PhNHCOPh	18.8	-.085	1.32	-4.8	
$PhNHCOCF_3$	12.6	.383	1.96	-14	
$PhNHSO_2Ph$	11.9	.136	1.35	-8.5	

[a] See footnote (a) and (g) in Table 1. [b] Experimental conditions are the same as described in footnote (b) of Table 1. [c] Derived using eqn. (2). [d] From ref. 9e.

aromaticity upon their formation. The high density of the positive charge and the strong tendency of resuming the more favored aromatic structure are most responsible for the high acidities of carbon radical cations. Table 3 also lists the $pK_{HA}^{+\bullet}$ values of arylacetonitrile radical cations for comparison. The difference in the magnitude of the substituent effect is worth noticing. For example, the p-MeO group causes a 2.6 pK unit acid-weakening effect on the acetanilide cation radical, as compared to a 13 pK unit decrease in acidity for the α-cyanobenzyl radical cation by the same substituent. This difference again originates from the difference in the positive charge distribution in the two aromatic systems.

EXPERIMENTAL SECTION

General. NMR spectra were obtained on a JEOL FX-90Q spectrometer. The purification of DMSO solvent and preparation of the dimsyl base were carried out according to the standard literature procedure.[14] The pK_A values of the neutral substrates were measured using the "Bordwell Indicator Overlapping Method"[14,15] on a Beckman DU-8B spectrophotometer. Melting points were taken with capillary melting-point tubes and are uncorrected. Tetrabutylammonium tetrafluoroborate (Aldrich) was recrystallized three times ($Et_2O/EtOH$) and vacuum-dried at 110°C for 10 h before use. Purity of other common reagents was verified by their known m.p.'s or b.p.'s or by spectral analysis, and if not satisfactory, recrystallization or distillation was performed.

Materials. Indicator compounds used in pK_A measurement and the substituted aniline substrates were synthesized according to literature or modified literature procedures. Details on synthesis and on the pK_{HA} measurement of the related substrates are reported elsewhere[18] and will not be repeated in this paper. The purity of all these compounds was ensured to be better than 99.9% by repeated recrystallization or chromatography. The starting materials used in these synthesis were either commercially available or prepared using published methods.

Electrochemical Measurements. Cyclic voltammograms were obtained on BAS-100B electrochemical analyzer (Purdue Research Park, West Lafayette, Indiana, USA) equipped with a three-electrode assembly. The working electrode was a 1.5 mm diameter platinum disk embedded in a cobalt glass seal and was polished consecutively with polishing alumina and diamond suspensions (supplied by BAS as a kit) between runs. The potentials were scanned at a sweep rate of 100 mV/s *vs.* the 0.1 M $AgNO_3/Ag$ (in 0.1 M Bu_4NBF_4-DMSO) reference electrode whose potential was periodically checked against the ferrocenium/ferrocene internal standard. A platinum wire was used as the auxiliary electrode. The nitranions were generated *in situ* under argon by titrating a stock dimsyl solution (enough to generate 1 mM anion concentration) into the solution containing the substrate and 0.1 M supporting electrolyte. The CV's were recorded on an HP 7475A digital plotter immediately following the nitranion generation and were reproducible to ±10mV. The potentials for neutral substrates were measured similarly which are generally reproducible to $\leq\pm20$ mV.

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